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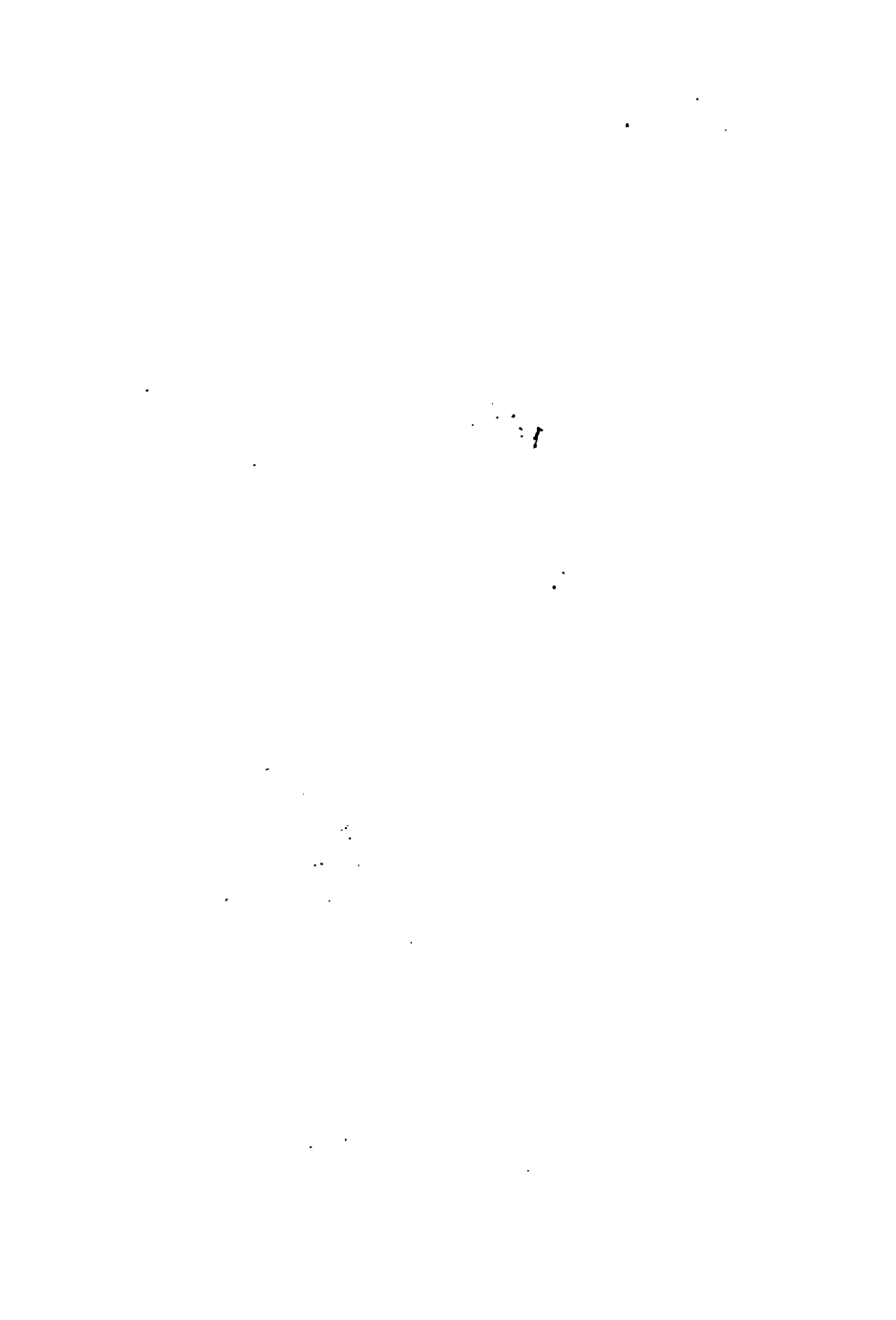
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# **ORGANIC CHEMISTRY :**

**ADAPTED FOR STUDENTS**

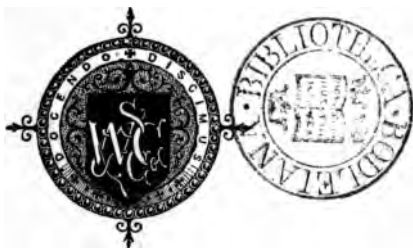
**IN THE**

**ELEMENTARY CLASSES OF THE SCIENCE AND ART DEPARTMENT  
SOUTH KENSINGTON.**

**BY**

**W. MARSHALL WATTS, D.Sc., F.C.S.,**

**PHYSICAL SCIENCE MASTER IN THE GIGGSWICK GRAMMAR SCHOOL.**



**LONDON AND GLASGOW :**

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**1873.**

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## P R E F A C E.

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A REFERENCE to the Syllabus of the Science and Art Department, will show that certain subjects treated of in the following pages, are not required at the examinations of the Department for the Elementary Stage. These extra subjects are contained in the following Sections:—§§ 2, 3, 25 to 29, 40 to 42, 50, 69 to 70, 76 to 78, 89 to 134.

*January, 1873.*

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# SYLLABUS

OF THE

## SCIENCE & ART DEPARTMENT.

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### SUBJECT XI.—ORGANIC CHEMISTRY.

#### ELEMENTARY COURSE.

Pupils presenting themselves for examination will be expected to possess a knowledge of the following subjects:—

Definition of organic bodies; their ultimate analysis (§ 1). Calculation of empirical formulæ. Compound organic radicals. Notation of organic compounds (§ 4). Graphic and symbolic formulæ (§ 4).

**ORGANIC RADICALS.**—Positive radicals. Preparation and properties of the monad radicals of the methyl series (§§ 5—12). Monad radicals of the vinyl and phenyl series (§§ 13—15).

Dyad positive radicals of the ethylene series (§§ 16—21). Preparation and properties of ethylene (§ 16).

Negative radicals. Cyanogen (§ 22). Oxatyl (§ 23). Oxalic acid, its preparation and properties (§ 24).

**HYDRIDES OF THE ORGANIC RADICALS** (§§ 30—36).—Methylic hydride or marsh gas (§ 30). Paraffin (§§ 37, 38). Benzol (§ 39). Cyanic hydride or hydrocyanic acid (§§ 43—45). Oxatylic hydride or formic acid (§ 46).

**THE ALCOHOLS.**—Definition of an alcohol (§ 47). Methylic alcohol (§ 48). Ethylic or common alcohol (§ 49). Phenylic alcohol or carbolic acid (§ 51).

**THE ETHERS.**—Definition (§ 52). Preparation and properties of ethylic ether (§ 53).

**THE HALOID ETHERS** (§§ 54—61).—Their constitution. Preparation and properties of ethylic chloride (§ 59) and iodide (§ 60).

## VI. SYLLABUS OF STUDY FOR THE DEPARTMENT

**NEW SUBSTANCES** §§ 4—57. — Their names and properties. Atomic weights § 58. Chemical analysis of all of them. Elements § 59.

**NEW LAWS** §§ 61—71. — Definition of an element and. Acetic acid § 72. Lactic acid § 73. Benzene and § 74.

**PHYSICAL STATES** — Definition and nomenclature of the physical states of the elements and §§ 75—86. Preparation and properties of acetic ether and lactic ether §§ 87—96.

The evidence of a good knowledge of chemical manipulation will be rewarded by special extra payments. See § XXXIX of the Directory. This knowledge will at present be tested by questions set with the ordinary examination paper in May, and the course of laboratory practice to which the questions will be confined will be the preparation of ethyl cyanide, cyanogen, oxalic acid, marsh gas, hydrocyanic acid, ethylic alcohol, ethylic ether, ethylic iodide, acetic acid, lactic acid, and ethylic acetate or acetic ether. The analytical detection of hydrocyanic acid, oxalic acid, tartaric acid, citric acid, and acetic acid.

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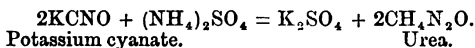
# ORGANIC CHEMISTRY.

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THE compounds of carbon with other elements, and in particular with hydrogen and oxygen, are so numerous that it is most convenient to make their study a special branch of Chemistry—**Organic Chemistry**. It is principally as a matter of convenience that these compounds are studied separately; it is very difficult to precisely define Organic Chemistry. The name indicates the idea formerly entertained that these substances could only be produced in living organisms; and Organic Chemistry was accordingly defined as the study of the products of animal and vegetable life. It was supposed that these substances could only be produced under the influence of a special "vital force." Now, while it is quite true that, in consequence of our ignorance of the processes which go on in the bodies of plants and animals—most organic substances are only obtained, directly or indirectly, from plants or animals—the possibility of artificially producing an organic substance has long been demonstrated, and we are slowly but steadily increasing the list of organic substances which have been produced artificially from their elements. The first organic substance which was obtained artificially was **Urea**, a substance occurring in the urine of animals. Urea contains  $\text{CH}_4\text{N}_2\text{O}$ , and thus contains the same elements as ammonium cyanate.

If nitrogen gas is passed over a mixture of charcoal and potassium carbonate at a bright red heat, potassium cyanide is formed; and if potassium cyanide is fused in a crucible with lead oxide, it takes up oxygen and is converted into potassium cyanate. Again, ammonia can be

formed by the direct combination of nitrogen and hydrogen. If, now, ammonium sulphate be mixed with potassium cyanate, the mixture dissolved in water, the solution evaporated to dryness and exhausted with alcohol, then the alcohol on evaporation leaves Urea, the following decomposition taking place:—



A second definition which has been proposed is, that Organic Chemistry is the Chemistry of **Compound Radicals**. A compound radical is a group of elements supposed to exist in each of the compounds of a series, and which is not itself easily decomposed in the various chemical changes which these compounds suffer. Thus, from alcohol,  $\text{C}_2\text{H}_5\text{O}$ , are obtained the following compounds:—ether,  $\text{C}_4\text{H}_{10}\text{O}$ ; hydrochloric ether,  $\text{C}_2\text{H}_5\text{Cl}$ ; sulphuric ether,  $\text{C}_4\text{H}_{10}\text{SO}_4$ ; nitric ether,  $\text{C}_2\text{H}_5\text{NO}_3$ ; hydrosulphuric ether,  $\text{C}_4\text{H}_{10}\text{S}$ ; mercaptan,  $\text{C}_2\text{H}_6\text{S}$ ; silicic ether,  $\text{C}_4\text{H}_{10}\text{SiO}_3$ . Each of these formulæ contains the group  $\text{C}_2\text{H}_5$ , and in all the chemical changes by which these different substances are obtained from alcohol, this group remains undecomposed. It is therefore a **Compound Radical**, and has received the name **Ethyl**. If we write the symbol E for  $\text{C}_2\text{H}_5$ , the connection of the different compounds with each other becomes plainer, and their parallelism with the salts of a metal such as potassium is evident. Thus,

Alcohol, .....	EHO	corresponding to	KHO	Potassium Hydroxide.
Ether, .....	$\text{E}_2\text{O}$	„	$\text{K}_2\text{O}$	Potassium Oxide.
Hydrochloric				
Ether, ....	$\text{ECl}$	„	KCl	Potassium Chloride.
Sulphuric				
Ether, ....	$\text{E}_2\text{SO}_4$	„	$\text{K}_2\text{SO}_4$	Potassium Sulphate.
Nitric Ether, .....	$\text{ENO}_3$	„	$\text{KNO}_3$	Potassium Nitrate.
Hydrosulphuric				
Ether, ....	$\text{E}_2\text{S}$	„	$\text{K}_2\text{S}$	Potassium Sulphide.
Mercaptan, ..	$\text{EHS}$	„	KHS	Potassium Hydrosulphide.
<i>Silicic Ether, <math>\text{E}_2\text{SiO}_3</math></i>		„	$\text{K}_2\text{SiO}_3$	Potassium Silicate.

This definition is, however, also incomplete ; for, while it is in Organic Chemistry that we have principally to do with compound radicals, yet in inorganic compounds also we consider compound radicals to exist. For example, the compound radical  $\text{SO}_2$  in the sulphates,  $\text{NO}_2$  in the nitrates, and so on.

The best definition which has been proposed is that which makes Organic Chemistry the study of the **carbon compounds**. The only objection to this is, that it is somewhat too extensive, and includes carbon monoxide, carbon dioxide, and a few other substances which are always regarded as inorganic.

There is thus no absolute character which distinguishes an organic substance from an inorganic substance. All organic substances contain carbon. Some contain only carbon and hydrogen; the vast majority contain carbon, hydrogen, and oxygen; and a smaller number contain carbon, hydrogen, oxygen, and nitrogen; sulphur, phosphorus, chlorine, iodine, bromine, boron, silicon, and the metals are occasional constituents of organic compounds.

Organic compounds are, as a rule, more complicated than inorganic substances, though some few have very simple formulæ. For example—

Hydrocyanic acid	contains	CHN.
Stearin	„ „	$\text{C}_{57}\text{H}_{110}\text{O}_6$ .
Albumen	„ „	$\text{C}_{72}\text{H}_{112}\text{N}_{18}\text{SO}_{22}$ .

**1. Analysis of Organic Substances.**—By the **proximate analysis** of an organic substance is meant its separation into the different substances which it contains. **Ultimate analysis** means the splitting up of these substances into their elements.

Thus, by a systematic process of distillation, petroleum is found to be a mixture of various hydrocarbons. These hydrocarbons, which have thus been separated by the proximate analysis, are shown by ultimate analysis to have the formulæ  $\text{C}_6\text{H}_{14}$ ,  $\text{C}_7\text{H}_{16}$ , &c.

The method of ultimate analysis is, with slight

modifications, the same for all organic substances whatever. It consists in burning completely a known weight of the substance, and ascertaining the weight of carbon dioxide and water produced. We obtain thus sufficient data if the substance contain only carbon and hydrogen, or only carbon, hydrogen, and oxygen; if the substance contain also nitrogen, chlorine, or other elements, these must be determined in separate experiments by special methods.

The organic substance may be burnt in a current of oxygen, but more commonly the combustion is effected by heating it together with copper oxide, which readily gives up its oxygen to the organic substance. We will suppose that the substance to be analyzed is a solid containing carbon, hydrogen, and oxygen—sugar, for example. As copper oxide absorbs moisture from the air, it is necessary that the oxide to be used should be heated strongly before the experiment. It is then transferred hot to a narrow-mouthed flask, which is immediately corked, so that the oxide cools out of contact with air. A hard glass tube, called a combustion tube, about 600 m.m. long, open at one end, and drawn out at the other to a fine point, is employed. Into this is introduced enough copper oxide to fill about 150 m.m. of the tube, and then about 0.3 gr. of the sugar to be analyzed. The sugar is weighed in a little glass tube, from which about this quantity is shaken out into the combustion tube. The tube is then weighed again, and the loss in weight of course gives the weight of sugar taken. The sugar is then thoroughly mixed with the oxide in the tube, by raking them up together with a wire, and the tube is then filled up with oxide.

The apparatus for collecting the water (*a*, fig. 1), a tube filled with calcium chloride, which has just been weighed, is then fitted to the combustion tube, by means of a good and dry cork, and then to this is attached by india-rubber tubing the apparatus for absorbing the carbon dioxide produced. This, which has also been weighed

just before the experiment, is shown in *b*, fig. 1 (Liebig's bulbs), and contains a solution of caustic potash. The combustion tube is then placed in a gas or charcoal furnace, so that it can be heated to redness, and the calcium chloride tube and potash bulbs are supported outside the furnace, so that they are shielded from the heat.

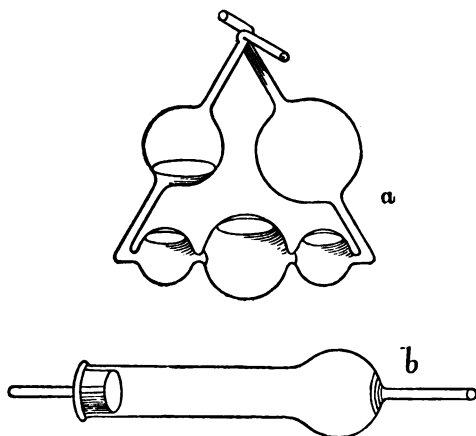


Fig. 1.

The front part of the tube containing the copper-oxide alone is first heated to redness, and then the rest of the tube is very gradually heated, commencing from behind. As soon as the part of the tube containing the mixture sugar and copper oxide gets hot, the sugar begins to burn, producing water and carbon dioxide, and these gases come off and are absorbed,—the water in the calcium chloride tube, and the carbon dioxide in the potash bulbs. When the sugar taken has been completely burned, and no more gas comes off, the point of the tube is broken off

The formula of carbon dioxide,  $\text{CO}_2$ , shows that 44 grs. contain 12 grs. carbon; or 11 grs. carbon dioxide contain 3 grs. carbon. The weight of carbon contained in the substance is therefore  $\frac{1}{11} \times 0.8947 = 0.2440$  gr. In like manner the weight of hydrogen is  $\frac{1}{8} \times 0.1602$  gr. = 0.0178 gr. Since benzoic acid contains only carbon, hydrogen, and oxygen, the difference between 0.355 and 0.2618 gr. (= 0.2440 + 0.0198) is the oxygen contained

in the weight of benzoic acid taken. Hence the composition of the substance is—

Carbon, .....	0.2440
Hydrogen, .....	0.0178
Oxygen, .....	0.0932
Benzoic acid, .....	0.3550

The next thing is to calculate the weight of each element contained in 100 grs. of the substance. We have thus the three proportions—

$$\begin{aligned} 0.3550 : 100 &:: 0.2440 : \text{percentage of carbon.} \\ 0.3550 : 100 &:: 0.0178 : \text{percentage of hydrogen.} \\ 0.3550 : 100 &:: 0.0938 : \text{percentage of oxygen.} \end{aligned}$$

We thus obtain—

Carbon, .....	68.74
Hydrogen, .....	5.01
Oxygen, .....	26.25
	100.00

We next divide these numbers by the atomic weights of the respective elements—

$$\frac{68.74}{12} = 5.731, \quad \frac{5.01}{1} = 5.01, \quad \frac{26.25}{16} = 1.64.$$

We next find the simplest whole numbers in the same proportion as their quotients, and we observe that 1.64 divided into 5.01 gives as quotient nearly 3; and that 1.64 divided into 5.73 gives nearly  $3\frac{1}{2}$ . Hence the formula is probably  $C_7H_6O_2$ .

It is indispensable, however, to check this result by comparing the percentage composition calculated from this formula with the percentage composition found by our analysis. Making this comparison, we have—

	Found.	Calculated.
Carbon, .....	68.74	68.86
Hydrogen, .....	5.01	4.91
Oxygen, .....	26.25	26.23
	100.00	100.00

The differences are not greater than those usually obtained in consequence of **experimental errors**. It is very difficult to burn the carbon completely without losing some carbon dioxide; and, again, it is scarcely possible to obtain the copper oxide absolutely dry. The percentage of carbon is thus always slightly less than it should be, and the percentage of hydrogen slightly **greater**; and the numbers calculated from the formula  $C_7H_6O_2$  agree sufficiently well with the numbers found by experiment.

There are two different methods of determining the quantity of nitrogen in an organic substance. The first of these depends upon the fact that most organic substances which contain nitrogen give it off as ammonia, when they are heated with an alkali. If, for example, a little albumen be heated in a test-tube with caustic potash, the smell of ammonia will easily be recognized. In order to determine the nitrogen by this method a weighed portion of the substance is mixed in a short combustion tube with a mixture of caustic soda and lime, known as **Soda-lime**. The ammonia which comes off is collected in a glass bulb of peculiar shape, which is fitted to the combustion tube by means of a good cork, and which contains hydrochloric acid. The ammonium chloride formed is precipitated with platinum chloride, and the precipitate,  $PtCl_4 \cdot 2NH_4Cl$ , collected and weighed. Or the precipitate may be heated to redness, and the platinum thus obtained weighed, and the process may then be used with substances which, instead of ammonia, give off organic bases—such as ethylamine. The formula of the precipitate would in this case be  $PtCl_4 \cdot 2NH_2C_2H_5Cl$ . But in each case 197.2 grs. platinum correspond to 28 of nitrogen.

The second method of determining nitrogen must be employed with some substances which contain nitrogen oxide, and do not give off the whole of the nitrogen in the form of ammonia. In this case a weighed quantity of the substance is burned in a combustion tube with *copper oxide*, and the front part of the tube is filled with

copper turnings, in order to insure that no nitrogen oxides come off. The nitrogen is then obtained in the free state, and collected and measured. From the volume we can of course easily calculate the weight of the nitrogen.

In every case the presence of nitrogen in a substance may be detected by heating the substance in a test-tube with a fragment of potassium. When cold, water is added, and a drop of ferrous sulphate, and the solution boiled. If, then, on adding excess of hydrochloric acid, a precipitate of Prussian blue is obtained, the presence of nitrogen is demonstrated.

Chlorine, bromine, and iodine are determined by heating the substance with caustic lime, dissolving the mass in nitric acid, adding silver nitrate, and weighing the precipitated silver chloride, bromide, or iodide. Phosphorus and sulphur are determined by heating the substance with a mixture of sodium carbonate and potassium nitrate, by which these elements are obtained as sulphate and phosphate, and are determined by the ordinary methods employed in inorganic analysis.

**2. Determination of the Rational Formula of an Organic Substance.**—The ultimate analysis of an organic substance gives us only its *empirical formula*, but gives us no information as to the *rational formula*.

The analysis of *acetic acid*, for example, shows us that its composition is that expressed by the formula  $\text{CH}_2\text{O}$ . But whether its true formula is  $\text{CH}_2\text{O}$ , or  $\text{C}_2\text{H}_4\text{O}_2$ , or  $\text{C}_3\text{H}_6\text{O}_3$ , or any other multiple of the first, can only be decided by further experiments, which determine its molecular weight. One of the most generally applicable methods of determining this point is to ascertain the specific gravity of the substance in the state of vapour. It is true of organic substances as of inorganic, that in the gaseous state their molecules occupy the same volume—viz., that occupied by  $\text{HH}$ ; and the vapour density of a compound, referred to hydrogen as unity, is expressed by half its molecular weight. If, for example,

the formula of acetic acid be  $\text{CH}_2\text{O}$ , then this weight—viz., 30, occupies the same volume as 2 of hydrogen, or acetic acid vapour must be 15 times heavier than hydrogen. If, however, it be found by experiment (as is the case) that acetic acid vapour is 30 times heavier than hydrogen, it will follow that the true formula is  $\text{C}_2\text{H}_4\text{O}_2$ .

There are two principal methods of determining the specific gravity of a vapour—the methods of Dumas and of Gay-Lussac. In the first we determine the weight of a certain volume of the vapour; in the second we determine the volume of a certain weight of the substance when in the state of vapour.

**3. Dumas' Method of Determining Vapour Densities.**—A glass globe of from 0.20 to 500 c.c. capacity is employed, the neck of which is drawn out to a point, as shown in the figure. The weight of this is ascertained, and a sufficient quantity of the liquid to be experimented on is introduced. The globe is then fixed in its place, and plunged into a bath of oil heated to a temperature some  $30^\circ$  or  $40^\circ$  above the boiling point of the liquid, so that only the fine point remains above the oil. The temperature of the bath is observed by means of the thermometer held by the other clamp.



Fig. 2.

The liquid then enters into ebullition, and a rapid stream of vapour issues from the bulb, completely expelling the air. At the moment that the rush of vapour ceases the point of the globe is melted together with the blow-pipe; and the temperature of the bath, and the height of the barometer are observed. The globe is

then removed from the bath, cleaned, and weighed again; the temperature in the balance case, and the height of the barometer being observed at this second weighing. Then the point of the globe is broken under mercury, and the weight or volume of the mercury which fills the globe determined, so as to ascertain the volume of the globe.

The method of calculation will be best explained by an example in which certain minor corrections (for expansion of glass, &c.) are omitted.

#### DETERMINATION OF VAPOUR DENSITY OF ACETIC ACID.

Weight of balloon and air,.....	22·8043 grs.
Weight of balloon filled with vapour, .....	22·9223 grs.
Temperature at weighing,.....	15° C.
Barometer at weighing,.....	750 m.m.
Temperature of bath, .....	150° C.
Barometer at time of sealing,.....	755 m.m.
Volume of balloon,.....	230 c.c.

The weight of the balloon, at the first weighing, is almost exactly the weight *in vacuo* of the glass of the balloon. But at the second weighing, in order to obtain the weight *in vacuo* of the balloon and vapour, we must add to the weight obtained the weight of the air displaced. This is very nearly the weight of 230 c.c. of air at 15° C. and 750 m.m. Now, 230 c.c. air at 15° C. and 750 m.m. become at 0° C. and 760 m.m.

$$\frac{230 \times 273 \times 750}{288 \times 760} \text{ or } 215\cdot15 \text{ c.c.};$$

and since one litre of air at standard pressure and temperature weighs 1·2936 gr., the weight of this air is  $215\cdot15 \times 0\cdot0012936$  gr., or 0·2783 gr. The weight of the vapour contained in the globe is then 22·9223 grs. + 0·2783 gr. = 22·8043 grs. or 0·3963 grs. We next require to know the weight of the same volume of hydrogen, measured under the same circumstances.

Now, 230 c.c. gas at 150° C. and 755 m.m. becomes at 0° C. and 760 m.m.  $\frac{230 \times 273 \times 755}{423 \times 760}$  or 147·46 c.c.,

and the volume of hydrogen weighs  $147.46 \times 0.0000896$  gr. or 0.01321 gr.

The specific gravity of the vapour in reference to hydrogen is therefore  $\frac{0.3963}{0.01321}$  or 30.

The method of Gay-Lussac is less frequently employed, and only for volatile liquids. A small quantity of the liquid is weighed out in a little glass bulb, which is then introduced into a graduated glass tube filled with mercury, and inverted in a trough of mercury. The whole apparatus is then heated to the necessary temperature by means of a water bath, in which it is immersed, and the volume occupied by the vapour determined.

In the case of an organic substance of acid or basic properties, the rational formula may be ascertained by the analysis of some one of its salts. To take the same example as before — that of acetic acid — the rational formula may be obtained by the analysis of silver acetate. If a weighed quantity of silver acetate be carefully heated in a crucible, it is decomposed, leaving a residue of metallic silver. It is found thus that silver acetate contains 64.68 per cent. of silver. The proportion  $64.68 : 108 :: 35.32$  gives us 58.98 for the atomic weight of the carbon hydrogen and oxygen contained in silver acetate, all taken together. But 108 of silver replace 1 of hydrogen. Hence the molecular weight of the acetic acid itself is  $58.98 + 1$ , or very nearly 60, the same as found before. As a second example, we will take succinic acid. Ultimate analysis shows that its composition is that expressed by the formula  $C_4H_4O_4$ , and it is found that its barium salt contains 54.15 per cent. of barium. The proportion  $54.15 : 137 :: 45.85$  gives us 116 for the molecular weight of the carbon, hydrogen, and oxygen it contains. As barium is a diatomic metal, and 137 parts by weight therefore replace 2 of hydrogen, it follows that the molecular weight of the acid is 118, and its formula is therefore  $C_4H_4O_4$ .

A similar method is available in the case of substances

possessed of basic properties. It is found, for example, that 0.4560 gr. quinine absorbs 0.1026 gr. hydrochloric acid, forming quinine hydrochlorate. The proportion  $0.1026 : 36.5 :: 0.4560$  gives 162.2 for the molecular weight of quinine. The analysis of quinine gives, for formula,  $C_{10}H_{12}NO$ , the molecular weight of which is 162; and this is, therefore, not only the empirical formula of quinine, but also its rational formula.

The salt selected for analysis in the case of many basic substances, which more or less resemble ammonia, is the double salt formed by the chloride with platinum chloride. These double salts are in most cases insoluble, or only sparingly soluble, and can therefore be easily obtained pure. They are also easily decomposed by simple heating, leaving behind only metallic platinum. Ammonium chloride forms with platinum chloride the salt  $PtCl_4 \cdot 2NH_4Cl$ ; and in the corresponding salts the organic base simply replaces the  $NH_4$ . For example, a base obtained from coal tar has the empirical formula  $C_8H_{11}N$ . When it is dissolved in hydrochloric acid, and platinum chloride is added, a double salt is obtained, which, on heating, leaves behind 30.16 per cent. of metallic platinum. The proportion  $30.16 : 197 :: 100$  gives us 653 for the molecular weight of this double salt. If the rational formula of the base be simply  $C_8H_{11}N$  (and not a multiple of  $C_8H_{11}N$ ), the formula of the double salt will be  $PtCl_4 \cdot 2C_8H_{11}NHCl$ , and this has for molecular weight 652, agreeing with the number just found.

In many cases the rational formula of a substance may be inferred from the decompositions which it undergoes. Thus the hydrocarbon obtained by decomposing potassium acetate by electricity has the composition represented by the formula  $CH_3$ . On subjecting it to the action of chlorine, however, it is found that six different compounds can be obtained from it—viz.,  $C_2H_5Cl$ ,  $C_2H_4Cl_2$ ,  $C_2H_3Cl_3$ ,  $C_2H_2Cl_4$ ,  $C_2HCl_5$ ,  $C_2Cl_6$ ; and, since the hydrogen can be displaced at six successive steps, the substance must con-

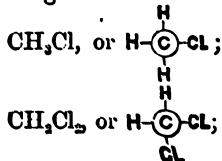
tain  $H_8$ , and not  $H_2$  only. The formula  $C_2H_6$  is confirmed by the determination of the vapour density.

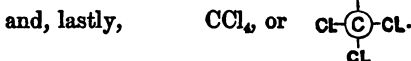
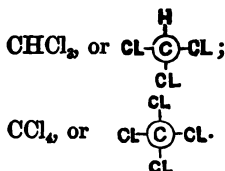
4. **Carbon**, the essential constituent of every organic substance, is a *tetratomic* element. By this is meant that an atom of carbon is *equivalent to*, or can take the place of *four* atoms of hydrogen, or of any monatomic element. Thus, if we compare the formulæ of carbon chloride and of hydrogen chloride, viz.,  $CCl_4$  and  $HCl$  (or  $H_4Cl_4$ ), we see that the atom of carbon occupies the places of four atoms of monatomic hydrogen. The same fact is seen in comparing the formulæ of carbon dioxide and water,  $CO_2$  and  $H_2O$  (or  $H_4O_2$ ). The atomicity of an element is thus measured by the number of atoms of a monatomic element it can displace, or with which it can combine. Thus, the formulæ of the compounds of chlorine, oxygen, nitrogen, and carbon, with hydrogen— $ClH$ ,  $OH$ ,  $NH_3$ ,  $CH_4$ —show at once the atomicities of these elements. These differences are denoted in *symbolic* formula by dashes and Roman numerals placed at the right of the symbol, as  $Cl'$ ,  $O''$ ,  $N'''$ ,  $C''''$ ; and in *graphical* formulæ, by the number of *bonds* or points of attachment with

which the atom is represented; as  $\textcircled{Cl}-$   $- \textcircled{O}-$   $\textcircled{N}-$   $\textcircled{C}-$   
The substance of which the *symbolic* formula is  $CH_4$ , and

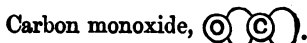
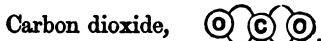
*graphic* formula  $\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$ , is marsh gas. The hydrogen it

contains can be displaced by chlorine, yielding compounds of carbon with both hydrogen and chlorine; and experiment shows that this displacement can be effected by four successive steps. Thus, by the action of chlorine on marsh gas, the following substances have been obtained:—

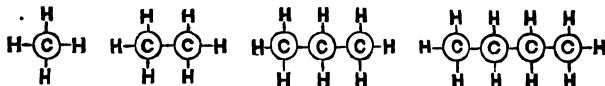




A tetratomic element may sometimes behave as a diatomic one. Thus, carbon is tetratomic in carbon dioxide, but diatomic in carbon monoxide. In this last case two of the four bonds of the carbon *satisfy each other*, and so become latent.



But no atom in any compound existing in the free state has any of its bonds unsatisfied. Two atoms of carbon may unite together, forming a nucleus which can combine with six atoms of hydrogen. So a group composed of three carbon atoms combines with eight atoms of hydrogen, a group of *four* with *ten*, and so on. This is rendered evident by the following graphical formulæ:—

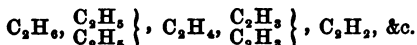


Any one of these compounds, in which all the bonds of the carbon atoms are satisfied by union with hydrogen, is called a *saturated* hydrocarbon; and we find, in practice, that these hydrocarbons do not combine with chlorine or other elements: but a hydrocarbon in which one or more bonds remain unsatisfied is *non-saturated*; and we find that such non-saturated hydrocarbons do combine readily with chlorine, bromine, &c. A group of atoms, in which only *one* bond remains unsatisfied is called a *monatomic* or *monad* radical; if two bonds are free, it is diatomic or a *dyad*; if three, *triatomic*, and so on.

Thus, for example, we have

Saturated hydrocarbon, .....	$C_2H_6$ .
Monatomic radical, .....	$C_2H_5$ .
Diatomic radical, .....	$C_2H_4$ .
Triatomic radical, .....	$C_2H_3$ .
Tetratomic radical, .....	$C_2H_2$ , &c.

Of these only  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ , &c., can exist in the free state. According to the rule just stated, that in no compound existing in the free state are there ever any bonds unsatisfied,  $C_2H_5$ ,  $C_2H_3$ , &c., can only exist in combination either with themselves or with some other group or element. So that the formulæ of the hydrocarbons in the free state are



Let us now return for a moment to the *chlorine substitution products* of marsh gas whose formulæ have already been given. They are all saturated compounds; but those containing chlorine may be regarded as the chlorides of organic radicals. Thus—

Saturated hydrocarbon, ....	$CH_4$	Marsh gas.
Chloride of monad radical, .....	$CH_3Cl$	Methyl chloride.
Chloride of dyad radical, ....	$CH_2Cl_2$	Methylene dichloride.
Chloride of triad radical, ...	$CHCl_3$	Chloroform.
Chloride of tetrad radical, .	$CCl_4$	Carbon tetrachloride.

In exactly the same way, the action of chlorine on the saturated hydrocarbon  $C_2H_6$  yields the compounds  $C_2H_5Cl$ ,  $C_2H_4Cl_2$ ,  $C_2H_3Cl_3$ ,  $C_2H_2Cl_4$ ,  $C_2HCl_5$ , and  $C_2Cl_6$ . Similar compounds can be obtained from the higher saturated hydrocarbons  $C_3H_8$ ,  $C_4H_{10}$ , &c.

We can then arrange these substances in the following series :—

Saturated Hydrocarbons.	Monad Radicals.	Dyad Radicals.
$CH_4$ , .....	Methyl, $CH_3$ , .....	Methylene, $CH_2$ .
$C_2H_6$ , .....	Ethyl, $C_2H_5$ , .....	Ethylene, $C_2H_4$ .
$C_3H_8$ , .....	Propyl, $C_3H_7$ , .....	Propylene, $C_3H_6$ .
$C_4H_{10}$ , .....	Butyl, $C_4H_9$ , .....	Butylene, $C_4H_8$ .
$C_5H_{12}$ , .....	Amyl, $C_5H_{11}$ , .....	Amylene, $C_5H_{10}$ .
&c.	&c.	&c.

Each of these series is termed a *homologous series*. It

will be remarked, that each term of a homologous series differs by  $\text{CH}_2$  from the one before it. The names given to the monad and dyad radicals in the preceding table are those usually employed. A complete system of naming all possible hydrocarbons has been proposed by Dr. Hofmann, and is given in the following tables :—

HYDROCARBONS OF EVEN ATOMICITY.				
Saturated.	Dyads.	Tetrads.	Hexads.	Octads.
Methane, $\text{CH}_4$ .	Methene, $\text{CH}_2$ .	—	—	—
Ethane, $\text{C}_2\text{H}_6$ .	Ethene, $\text{C}_2\text{H}_4$ .	Ethine, $\text{C}_2\text{H}_2$ .	—	—
Propane, $\text{C}_3\text{H}_8$ .	Propene, $\text{C}_3\text{H}_6$ .	Propine, $\text{C}_3\text{H}_4$ .	Propone, $\text{C}_3\text{H}_2$ .	—
Quartane, $\text{C}_4\text{H}_{10}$ .	Quartene, $\text{C}_4\text{H}_8$ .	Quartine, $\text{C}_4\text{H}_6$ .	Quartone, $\text{C}_4\text{H}_4$ .	Quartune, $\text{C}_4\text{H}_2$ .
RADICALS OF UNEVEN ATOMICITY.				
Monads.	Triads.	Pentads.	Heptads.	Enneads.
Methyl, $\text{CH}_3$ .	Methenyl, $\text{CH}$ .	—	—	—
Ethyl, $\text{C}_2\text{H}_5$ .	Ethenyl, $\text{C}_2\text{H}_3$ .	Ethinyl, $\text{C}_2\text{H}$ .	—	—
Propyl, $\text{C}_3\text{H}_7$ .	Propenyl, $\text{C}_3\text{H}_5$ .	Propinyl, $\text{C}_3\text{H}_3$ .	Proponyl, $\text{C}_3\text{H}$ .	—
Quartyl, $\text{C}_4\text{H}_9$ .	Quartenyl, $\text{C}_4\text{H}_7$ .	Quartinyl, $\text{C}_4\text{H}_5$ .	Quartonyl, $\text{C}_4\text{H}_3$ .	Quartunyl, $\text{C}_4\text{H}$ .

The organic radicals, like the elements, are classified into *Negative* or *Chlorous*, and into *Positive* or *Basylous*. When water is decomposed by electricity, the hydrogen comes off at the negative pole, and the oxygen at the positive. Hence *hydrogen* is termed a *positive element*, and oxygen a *negative element*. In like manner potassium, sodium, silver, and other metals, belong to the positive or basylous group; and chlorine, bromine, iodine, and sulphur, to the negative or chlorous group. Of organic radicals, methyl, ethyl, ethylene, &c., are positive, whilst cyanogen,  $\text{CN}$ , and oxatyl,  $\text{CO}_2\text{H}$ , are negative radicals.

**5. Monad Radicals of the Methyl Series.**—We have seen that the hydrocarbons  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , &c., can only exist in combination. Just as the molecule of free hydrogen

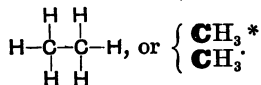
contains  $\left. \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \right\}$ , so the formula of free methyl is  $\left. \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix} \right\}$ ; of free ethyl,  $\left. \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{smallmatrix} \right\}$ ; &c.

It has been shown that these radicals are identical with certain members of the series, to be afterwards described, of the hydrides of the organic radicals, thus—

Methyl,	$\left. \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix} \right\}$	is identical with	Ethyl hydride, .....	$\left. \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{H} \end{smallmatrix} \right\}$
Ethyl,	$\left. \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{smallmatrix} \right\}$	„ „	Butyl hydride, .....	$\left. \begin{smallmatrix} \text{C}_4\text{H}_9 \\ \text{H} \end{smallmatrix} \right\}$
Propyl,	$\left. \begin{smallmatrix} \text{C}_3\text{H}_7 \\ \text{C}_3\text{H}_7 \end{smallmatrix} \right\}$	„ „	Hexyl hydride, .....	$\left. \begin{smallmatrix} \text{C}_6\text{H}_{11} \\ \text{H} \end{smallmatrix} \right\}$
Butyl,	$\left. \begin{smallmatrix} \text{C}_4\text{H}_9 \\ \text{C}_4\text{H}_9 \end{smallmatrix} \right\}$	„ „	Octyl hydride, .....	$\left. \begin{smallmatrix} \text{C}_8\text{H}_{17} \\ \text{H} \end{smallmatrix} \right\}$
Amyl,	$\left. \begin{smallmatrix} \text{C}_5\text{H}_{11} \\ \text{C}_5\text{H}_{11} \end{smallmatrix} \right\}$	„ „	Decatyl hydride, .....	$\left. \begin{smallmatrix} \text{C}_{10}\text{H}_{21} \\ \text{H} \end{smallmatrix} \right\}$
Hexyl,	$\left. \begin{smallmatrix} \text{C}_6\text{H}_{13} \\ \text{C}_6\text{H}_{13} \end{smallmatrix} \right\}$	„ „	Dodecatyl hydride, ..	$\left. \begin{smallmatrix} \text{C}_{12}\text{H}_{25} \\ \text{H} \end{smallmatrix} \right\}$
Heptyl,	$\left. \begin{smallmatrix} \text{C}_7\text{H}_{15} \\ \text{C}_7\text{H}_{15} \end{smallmatrix} \right\}$	„ „	Tetradecatyl hydride,	$\left. \begin{smallmatrix} \text{C}_{14}\text{H}_{29} \\ \text{H} \end{smallmatrix} \right\}$
Octyl,	$\left. \begin{smallmatrix} \text{C}_8\text{H}_{17} \\ \text{C}_8\text{H}_{17} \end{smallmatrix} \right\}$	„ „	Hexadecatyl hydride,	$\left. \begin{smallmatrix} \text{C}_{16}\text{H}_{33} \\ \text{H} \end{smallmatrix} \right\}$

The above are the only hydrocarbons of this series which have been prepared.

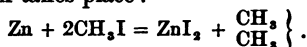
**6. Methyl.**—Ethyl hydride or ethane. Graphical formula :



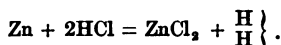
This compound is a gas, without taste or smell, which does not dissolve in water, but dissolves in alcohol to

\* This is simply an abbreviated form of the first formula. The element whose symbol is written first, **C**, is understood to be directly united with all the active bonds of the elements (or compound radicals) following on the same line; and the two carbon atoms are understood to be directly united together. It

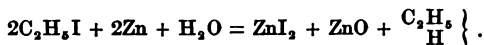
some extent. It may be prepared by heating together methyl iodide and zinc in a closed glass tube. The following reaction takes place :—



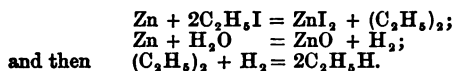
It will be observed that this reaction is exactly like that of zinc on hydrochloric acid :—



As thus obtained, the gas would be regarded as *methyl*. If we heat zinc together with ethyl iodide and water in a closed tube, the following reaction takes place :—



And, as thus obtained, the gas would be regarded as ethyl hydride. We may consider the reaction as taking place in two stages :—



But this *ethyl hydride* is in no way different from the *methyl* obtained by the first method. Methyl and ethyl hydride are then not merely *isomeric* (two substances which have different properties but the same formula are called *isomeric*, as acetic ether,  $\text{C}_2\text{H}_4\text{O}$ , and ethylene oxide,  $\text{C}_2\text{H}_4\text{O}$ ), but identical. Another interesting me-

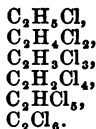
may be useful to give the formulæ of some well known inorganic substances in this abbreviated graphic notation :—

Water, .....	$\text{OH}_2$ .
Potassium hydrate, .....	$\text{OKH}$ .
Nitric acid, .....	$\text{NO}_2\text{Ho}$ .
Potassium nitrate, .....	$\text{NO}_2\text{Ko}$ .
Sulphuric acid, .....	$\text{SO}_2\text{Ho}_2$ .
Potassium sulphate, .....	$\text{SO}_2\text{Ko}_2$ .
Barium sulphate, .....	$\text{SO}_2\text{BaO}''$ .
Barium hydrate, .....	$\text{BaHo}_2$ .
Hydrogen potassium carbonate, .....	$\text{COHoKo}$ .
Phosphoric acid, .....	$\text{POHo}_3$ .

thod of obtaining methyl is by decomposing a solution of potassium acetate with the current of electricity from a galvanic battery. The formula of potassium acetate is  $\text{KC}_2\text{H}_3\text{O}_2$ , and it splits up first of all into K and  $\text{C}_2\text{H}_3\text{O}_2$ . This group, however, decomposes immediately into  $\text{CO}_2$  and  $\text{CH}_3$ ; and the potassium decomposes water, giving off hydrogen. The final result is thus the evolution of hydrogen at the one pole, and of carbon dioxide and methyl at the other pole.

Methyl is a little heavier than air. This can easily be discovered from the formula  $\text{C}_2\text{H}_6$ ; for the molecular weight being 30, it follows that methyl is 15 times as heavy as the same volume of hydrogen. But the specific gravity of hydrogen in reference to air as unity is 0.0693, and hence the specific gravity of methyl is  $15 \times 0.0693 = 1.0395$ . In the same way the weight of 1 litre of this gas at  $0^\circ \text{C}$ . and 760 m.m. pressure is  $15 \times 0.0896 = 1.344$  gr.

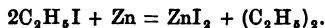
When methyl is mixed with chlorine no action takes place in the dark, but in sunlight the two react, producing a mixture of substances, which are *chlorine substitution products* of methyl. We obtain thus the following series:—



Corresponding to the series mentioned on p. 22, as obtained from marsh gas.

The first member of this series is ordinary ethyl chloride, from which common alcohol has been prepared, showing that the so-called methyl is really ethyl hydride.

7. *Ethyl*.—Butyl hydride or quartane,  $(\text{C}_2\text{H}_5)_2$ , or  $\left\{ \begin{array}{l} \text{CH}_2(\text{CH}_3) \\ \text{CH}_2(\text{CH}_3) \end{array} \right\}$ , is obtained by the action of zinc on ethyl iodide—



The decomposition is effected in strong sealed glass tubes.

A strong tube is filled with thin strips of zinc, and drawn out at the top before the blowpipe. Ethyl iodide is then introduced by heating the tube and cooling it, while the open extremity dips below the surface of the liquid. The tube is then exhausted by the air-pump, and sealed before the blowpipe. The tube is then heated for several hours in an oil bath, first to  $100^{\circ}$  C. only, and then to about  $135^{\circ}$ . Besides ethyl, there are produced in this process *ethylene* and ethyl hydride. When the tube is cooled in a freezing mixture, and the point then broken off under water, gas escapes, which at first is principally ethyl hydride and ethylene. The ethyl, being least volatile, comes off last, and is collected in a gas holder. Ethyl is a gas which burns with a white luminous flame. It condenses to a liquid at a few degrees below the freezing point. It is twice as heavy as air, or 29 times as heavy as hydrogen.

8. Propyl.—Hexyl hydride or sextane,  $(C_3H_7)_2$  or  $\left\{ \begin{array}{l} CH_2(C_2H_5) \\ CH_2(C_2H_5) \end{array} \right\}$ , is a liquid boiling at  $68^{\circ}$  C. It occurs, together with most of the other radicals of this series, in American petroleum.

9. Butyl,  $(C_4H_9)_2$ , boils at about  $117^{\circ}$ .

10. Amyl,  $(C_5H_{11})_2$ , boils at about  $161^{\circ}$ .

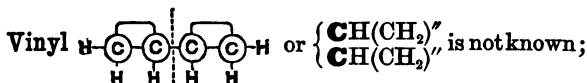
11. Hexyl,  $(C_6H_{13})_2$ , at about  $198^{\circ}$ .

12. Heptyl,  $(C_7H_{15})_2$ , at about  $238^{\circ}$ .

It will be noticed that the boiling point rises as we pass up the series; the higher the molecular weight, the higher the boiling point.

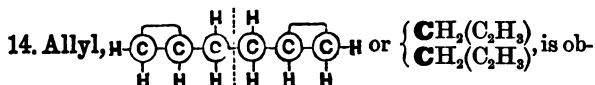
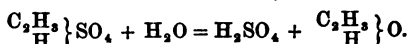
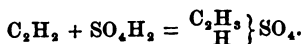
This is a general rule to which there are only a few exceptions.

13. Monad Radicals of the Vinyl Series:—

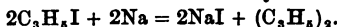


but vinyl alcohol,  $\left. \begin{array}{c} C_2H_3 \\ H \end{array} \right\} O$ , has been obtained by dis-

solving acetylene in sulphuric acid, and distilling the liquid with water—



tained by the action of sodium on allyl iodide,

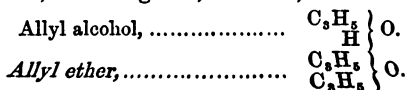


It is a liquid, of specific gravity 0.684, and boiling at  $59^\circ \text{C}$ ., which possesses a strong smell resembling that of radishes.

Allyl forms an alcohol corresponding to vinyl alcohol, of which the formula is  $\left\{ \begin{array}{c} \text{C}_3\text{H}_5 \\ \text{H} \end{array} \right\} \text{O}$ .

The group  $\text{C}_3\text{H}_5$  is thus monatomic, but we see from the graphical formulæ that two carbon bonds are united together. If these were active,  $\text{C}_3\text{H}_5$  would be a triad, as we see by comparing its formula with that of the saturated hydrocarbon,  $\text{C}_3\text{H}_8$ . Thus,  $\text{C}_3\text{H}_7$  is a monad,  $\text{C}_3\text{H}_9$  a dyad, and  $\text{C}_3\text{H}_8$  a triad; and it exists as such in *glycerine*, which is an alcohol formed on the type of three atoms of water. Glycerine has the formula  $\left\{ \begin{array}{c} \text{C}_3\text{H}_5 \\ \text{H}_3 \end{array} \right\} \text{O}_3$ , and it is

from glycerine that allyl iodide is obtained, two bonds of carbon becoming latent in the process. Allyl itself combines directly with bromine, and takes up four atoms—each of the bonds which are latent in allyl taking up one atom of bromine, and forming  $\text{C}_3\text{H}_7\text{Br}_4$ . Allyl forms a series of compounds, of which the following are the most important. Some of them exist naturally in certain plants, such as garlic, mustard, and horse-radish.



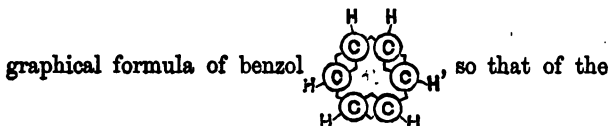
Allyl sulphide, .....	$\left. \begin{array}{l} \text{C}_3\text{H}_5 \\ \text{C}_3\text{H}_5 \\ \text{C}_3\text{H}_5 \end{array} \right\}$	S, Oil of garlic.
Allyl sulphocyanide, .....	$\left. \begin{array}{l} \text{C}_3\text{H}_5 \\ \text{CN} \end{array} \right\}$	S, Oil of mustard.

### 15. Monad Radicals of the Phenyl Series:—

Phenyl,  $\text{C}_6\text{H}_5$ , is the radical contained in the well-known hydrocarbon *benzol* or *benzine*, which is phenyl hydride  $\text{C}_6\text{H}_6$ . The radicals of this series have not been obtained in the free state. Benzol is the first term of a homologous series:—

Benzol, .....	$\text{C}_6\text{H}_6$ .
Tolnol, .....	$\text{C}_7\text{H}_8$ .
Xylol, .....	$\text{C}_8\text{H}_{10}$ .
Cumol, .....	$\text{C}_9\text{H}_{12}$ .
Cymol, .....	$\text{C}_{10}\text{H}_{14}$ .

These compounds must all be considered as derivatives of benzol, in which the carbon atoms are united in an altogether peculiar manner, as shown in the following



twenty-four bonds which the six carbon atoms have amongst them eighteen are used up in uniting the carbon atoms together, and only six remain free to combine with hydrogen or other elements. The substances in which this arrangement obtains constitute the "aromatic series."

The most important compounds of phenyl are the following:—

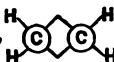
Benzol, .....	$\left. \begin{array}{l} \text{C}_6\text{H}_5 \\ \text{H} \end{array} \right\}$	
Carbolic acid or phenol, .....	$\left. \begin{array}{l} \text{C}_6\text{H}_5 \\ \text{H} \end{array} \right\}$	O.
Aniline, .....	$\left. \begin{array}{l} \text{C}_6\text{H}_5 \\ \text{H} \end{array} \right\}$	N.

*Phenyl* acts therefore like a monatomic alcohol radical;

nevertheless, there is a marked difference between its behaviour and that of the true alcohol-radicals, and the derivatives of benzol must be considered rather as substitution products derived by replacing one or more atoms of hydrogen in the original chain by the monatomic groups HO, NH<sub>2</sub>, &c. In this way also the homologues of benzol are formed, and we have consequently a large number of *isomeric* substances.\*

16. **Dyad Positive Radicals of the Ethylene Series.**—The radicals of this series (also called the *olefine* series), which have been obtained, are the following:—

	Boiling Point.
Ethylene,.....C <sub>2</sub> H <sub>4</sub> .	—
Propylene,.....C <sub>3</sub> H <sub>6</sub> .	—
Butylene,.....C <sub>4</sub> H <sub>8</sub> .	3°C.
Amylene,.....C <sub>5</sub> H <sub>10</sub> .	35°
Hexylene,.....C <sub>6</sub> H <sub>12</sub> .	69°
Heptylene,.....C <sub>7</sub> H <sub>14</sub> .	100°
Octylene,.....C <sub>8</sub> H <sub>16</sub> .	125°
Decatylene,.....C <sub>10</sub> H <sub>20</sub> .	160°
Cetene,.....C <sub>16</sub> H <sub>32</sub> .	275°
Cerotene,.....C <sub>27</sub> H <sub>54</sub> .	—
Melene,.....C <sub>36</sub> H <sub>72</sub> .	—

17. **Ethylene, orethene,**  or {  $\begin{matrix} \text{CH}_2 \\ \text{CH}_2 \end{matrix}$  }, is obtained by heating together alcohol and sulphuric acid. The equation representing the action is



\* The following hydrocarbons in this series are known:—

C<sub>6</sub>H<sub>6</sub>, Benzol.

C<sub>7</sub>H<sub>8</sub>, Methyl-benzol.

C<sub>8</sub>H<sub>10</sub>, Dimethyl-benzol, and Ethyl-benzol.

C<sub>9</sub>H<sub>12</sub>, Trimethyl-benzol, Methyl-ethyl-benzol, and Propyl-benzol.

C<sub>10</sub>H<sub>14</sub>, Tetra-methyl-benzol, Dimethyl-ethyl-benzol, Methyl-propyl-benzol, Diethyl-benzol.

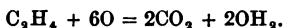
C<sub>11</sub>H<sub>16</sub>, Amyl-benzol.

C<sub>12</sub>H<sub>18</sub>, Amyl-tolnol.

For further information on this subject the larger manuals must be consulted.

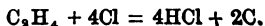
Alcohol is mixed with three or four times its volume of concentrated sulphuric acid. As the mixture has a tendency to froth up during the process, a good large flask should be taken, and the frothing may be checked considerably by half filling the flask with coarse sand. The mixture of alcohol and sulphuric acid is made slowly in a beaker, and then poured on to the sand, and the cork and exit-tube adapted to the flask, which is then heated in a sand bath. The gas may be collected over water in the ordinary way; but, if it be required pure, it must be made to pass through two wash bottles, the first containing concentrated sulphuric acid, and the second caustic soda. These substances absorb ether, alcohol vapour, sulphur dioxide, and carbon dioxide, which come off as impurities.

Ethylene is a colourless gas, of a peculiar smell. It burns in the air with a bright white flame, forming carbon dioxide and water. If mixed in a soda-water bottle with oxygen, it explodes violently when a light is put to the mixture. The proportions of ethylene and oxygen to be mixed can be found from the equation—

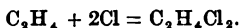


$\text{C}_2\text{H}_4$  means 28 parts by weight of ethylene, and O means 16 parts by weight of oxygen. If we take as unit-volume the volume occupied by 1 gr. of hydrogen, then O occupies 1 vol., and  $\text{C}_2\text{H}_4$  occupies 2 vols. We must therefore mix 1 vol. of ethylene with 3 vols. of oxygen.

Ethylene is 14 times heavier than hydrogen, and therefore  $14 \times 0.0693$  or 0.97 times heavier than air; and 1 litre weighs  $14 \times 0.0896$  or 1.2544 gr. The gas can be reduced to a liquid by pressure and cold. A mixture of ethylene with twice its volume of chlorine burns when a light is put to it, producing a dense cloud of black smoke. The chlorine combines with the hydrogen of the ethylene, and the carbon is separated according to the equation—



If a mixture of ethylene with its own volume of chlorine be exposed to daylight, the two gases combine rapidly, forming the compound,  $C_2H_4Cl_2$ , ethylene dichloride, or Dutch liquid.



The combination goes on less rapidly in the dark. The compound  $C_2H_4Cl_2$ , which was discovered in 1795 by some Dutch chemists, is a colourless liquid, smelling like chloroform, possessing a specific gravity of 1.271, and boiling at  $85^\circ C$ . By treatment with a solution of potassium hydroxide in alcohol, it yields *vinyl chloride*,  $C_2H_3Cl$ —



Vinyl chloride combines again with chlorine, forming  $C_2H_3Cl_2$ .



And by repeating the treatment with potash and chlorine the following compounds have been obtained, with which is compared the *isomeric* series from ethyl-hydride, mentioned on p. 28.

From Ethylene.	From Ethyl hydride.
Boiling Point.	Boiling Point.
$C_2H_4Cl_2$ , ..... $85^\circ C$ .	$C_2H_4Cl_2$ , ..... $58^\circ C$ .
$C_2H_3Cl_2$ , ..... $115^\circ C$ .	$C_2H_3Cl_3$ , ..... $75^\circ C$ .
$C_2H_2Cl_4$ , ..... $137^\circ C$ .	$C_2H_2Cl_4$ , ..... $102^\circ C$ .
$C_2HCl_5$ , ..... $154^\circ C$ .	$C_2HCl_5$ , ..... $154^\circ C$ .
$C_2Cl_6$ , ..... $182^\circ C$ .	$C_2Cl_6$ , ..... $182^\circ C$ .

When ethylene is continuously shaken with sulphuric acid, it is dissolved, forming ethyl sulphuric acid  $C_2H_5 \left. \begin{smallmatrix} \text{H} \end{smallmatrix} \right\} SO_4$ , and if this be diluted with water and distilled, alcohol is obtained. Thus, alcohol can be reproduced from ethylene.

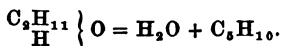
The ethyl compounds were compared (p. 10) with the potassium compounds. In like manner the compounds of *ethylene* may be compared with the salts of the diatomic *metal barium*. Thus—

Dutch liquid, .....	$C_2H_4Cl_2$ .	Barium chloride, $BaCl_2$ .
Ethylene alcohol	} $C_2H_4Ho_2$ .	Barium hydrate, $BaHo_2$ .
or glycol, .....		
Ethylene oxide, .....	$C_2H_4O$ .	Barium oxide, ... $BaO$ .
Ethylene nitrate, ...	$C_2H_4_2NO_3$ .	Barium nitrate, ... $Ba_2NO_3$ .

18. **Propylene**,  $C_3H_6$ , is a gas, much like ethylene, obtained by the action of sulphuric acid on propyl alcohol.

19. **Butylene**,  $C_4H_8$ , is a gas, which condenses to a liquid at  $3^\circ C$ . Ethylene, and, in smaller quantity, propylene and butylene, are constituents of ordinary coal gas.

20. **Amylene**,  $C_6H_{10}$ , is a colourless, very volatile liquid, resembling ether, with a smell resembling apples. It is best obtained by distilling amyl alcohol with zinc chloride, which, like sulphuric acid, has a very strong affinity for water—



21. **Hexylene**, **heptylene**, **octylene**, and **decatylene** are obtained by similar methods. **Cetene**, **cerotene**, and **melene** are obtained from various kinds of wax. The last two are solid bodies.

22. **Cyanogen** is a *negative* or *chlorous radical*, having the greatest resemblance in its chemical behaviour to the elements chlorine, bromine, and iodine, which, in the electrolysis of their salts, are evolved at the positive pole, or that connected with the copper or platinum of the battery.

Cyanogen gas is obtained by heating the cyanide of silver or of mercury. Mercury cyanide is easily obtained by dissolving mercury oxide in aqueous hydrocyanic acid. (The method of preparing hydrocyanic acid is described farther on.) On evaporating the solution, the salt crystallizes out. In order to prepare the gas, dry mercury cyanide in powder is heated in a tube or small flask made of difficultly fusible glass. The arrangement for the purpose is represented in figure 3. The gas must be collected

over mercury, as it is soluble in water. The decomposition which takes place is represented by the equation

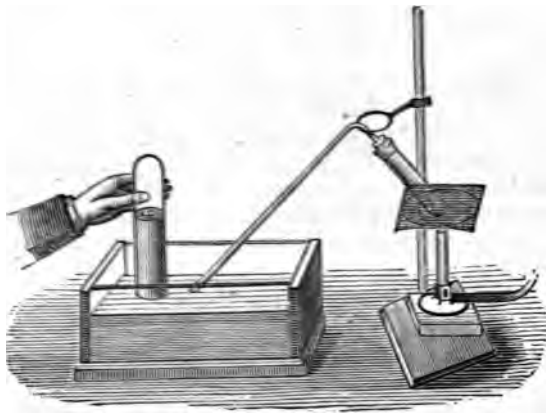
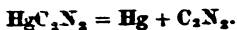


Fig. 3.

It must be observed, however, that very much less cyanogen is actually obtained than corresponds to the above equation, as a considerable proportion remains behind in the tube, in the form of a brown solid substance called paracyanogen. This substance has perhaps the formula  $\text{C}_6\text{N}_6$ , and is said to be a *polymer* or *polymeric modification* of cyanogen. By continuous heating it can be resolved into the gas.

The cyanogen thus obtained is a colourless gas of a peculiar faintly peach-like smell. It should not, however, be too strongly smelt, as it is poisonous. It is easily condensed to a liquid, at the ordinary temperature, under a pressure of only 2 or 3 atmospheres, or at the ordinary pressure, by a temperature of  $-21^\circ\text{C}$ . Liquid

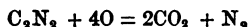
cyanogen is a colourless fluid, boiling, of course, at  $-21^{\circ}\text{C}$ ., and freezing at  $-34^{\circ}$  to a white solid. One volume of cold water dissolves 4 or 5 volumes of cyanogen gas, and in alcohol it is still more soluble.

Cyanogen gas is found by experiment to be 1.94 times heavier than air, or  $\left(\frac{1.94}{0.0693} = \right)$  28 times heavier than hydrogen. Hence, according to the law that "equal volumes of gases contain equal numbers of molecules," since the molecule of hydrogen contains  $\text{H}_2$ , the molecule of cyanogen contains  $\text{C}_2\text{N}_2$ , its graphical formula being



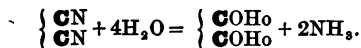
A litre of cyanogen weighs  $28 \times 0.0896 \text{ gr.} = 2.5088 \text{ grs.}$

Cyanogen burns in air with a splendid violet flame, and in oxygen still more brilliantly. The equation

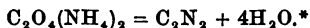


shows that 2 vols. of cyanogen require for complete combustion 4 vols. of oxygen, producing 4 vols. carbon dioxide and 2 vols. nitrogen.

23. *Oxatyl*, or carboxyl,  $\text{CO}_2\text{H}$ , is a radical which exists in all acids, and in the free state as  $(\text{CO}_2\text{H})_2$ , constitutes *oxalic acid*. A reaction, which is interesting as showing its connection with cyanogen, is that which takes place spontaneously when an aqueous solution of cyanogen is kept, by which the cyanogen is converted into ammonium oxalate. We may represent the decomposition by the equation—



Conversely, when ammonium oxalate is heated with phosphoric anhydride, it loses water, and yields cyanogen—



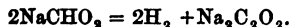
\* Oxalic acid can also be obtained from *formic acid*, to be

**24. Oxalic acid** can be obtained by the oxidation of many organic substances. It used to be obtained by the oxidation of sugar, but is now obtained on the large scale by the oxidation of sawdust. In order to prepare pure oxalic acid on the small scale, 10 grs. of powdered sugar may be heated in a flask with 75 c.c. strong nitric acid. When the evolution of nitrous fumes ceases, the liquid may be evaporated, till a drop taken out deposits crystals on cooling, and it may then be left to cool. Oxalic acid then separates out in transparent crystals, which contain  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .

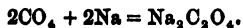
In the manufacture of oxalic acid from wood, the sawdust is mixed with a strong solution of caustic alkali (a mixture of one equivalent potassium hydrate and two equivalents sodium hydrate) and the pasty mass is heated on iron plates. The wood is decomposed and hydrogen escapes. When the mass is quite dry, it is treated with warm water, and the difficultly soluble sodium oxalate which is left behind is decomposed by boiling it with milk of lime. The calcium oxalate so obtained is decomposed by dilute sulphuric acid, and the solution of oxalic acid crystallized.

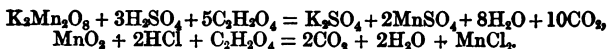
Oxalic acid crystallizes in prisms,  $\text{C}_2\text{O}_4\text{H}_2 \cdot 2\text{H}_2\text{O}$ , which, at  $100^\circ \text{C}$ ., lose their water of crystallization, and crumble down into a white powder. When heated, oxalic acid is decomposed without blackening, giving off carbon dioxide, carbon monoxide, water, and other products. It is decomposed into water and carbon dioxide by treatment with oxidizing agents; for example, with potassium permanganate, or with manganese dioxide and a dilute acid.

afterwards mentioned. If sodium formiate be heated, hydrogen is given off, and sodium oxalate is formed.



It can be produced from carbon dioxide by heating that gas, together with sodium, to a temperature equal to the boiling point of mercury, or  $360^\circ$ .





Treated with strong sulphuric acid oxalic acid gives off a mixture of equal volumes of carbon dioxide and carbon monoxide—



and the mixture of gases burns with a feeble blue flame.

Oxalic acid is a *dibasic* acid. Its most important salts are the following :—

*Potassium oxalate*,  $\text{C}_2\text{O}_4\text{K}_2\text{H}_2\text{O}$ , easily soluble in water.

*Potassium binoxalate*,  $\text{C}_2\text{O}_4\text{KH}$ ,  $\text{H}_2\text{O}$ , difficultly soluble in water ; occurs in some plants in the different species of oxalis and rumex, commonly known as *salts of lemon*.

*Calcium oxalate*,  $\text{C}_2\text{O}_4\text{Ca}$ , is very insoluble in water, and is precipitated when even a very dilute solution of an oxalate is mixed with neutral calcium chloride solution. The precipitate is insoluble in acetic acid, but easily soluble in hydrochloric or nitric acid. If the dry precipitate is heated to redness in a crucible, it is converted, without blackening, into calcium carbonate, which effervesces on addition of an acid, giving off carbon dioxide.

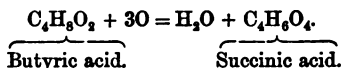
The *oxalates* of *barium*, *lead*, *mercury*, and *silver* are insoluble in water.

Oxalic acid forms the first term of a series of dibasic acids, of which the following are known :—

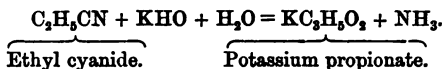
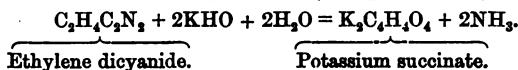
Oxalic, .....	$\text{C}_2\text{H}_2\text{O}_4$ .
Malonic, .....	$\text{C}_3\text{H}_4\text{O}_4$ .
Succinic, .....	$\text{C}_4\text{H}_6\text{O}_4$ .
Pyrotartaric, .....	$\text{C}_5\text{H}_8\text{O}_4$ .
Adipic, .....	$\text{C}_6\text{H}_{10}\text{O}_4$ .
Pimelic, .....	$\text{C}_7\text{H}_{12}\text{O}_4$ .
Suberic, .....	$\text{C}_8\text{H}_{14}\text{O}_4$ .
Azelaic, .....	$\text{C}_9\text{H}_{16}\text{O}_4$ .
Sebacic, .....	$\text{C}_{10}\text{H}_{18}\text{O}_4$ .
Brassylic, .....	$\text{C}_{11}\text{H}_{20}\text{O}_4$ .
Rocellic, .....	$\text{C}_{17}\text{H}_{32}\text{O}_4$ .

25. Succinic acid,  $\text{C}_4\text{H}_6\text{O}_4$ , is contained in amber, whence its name. It is an oxidation product of many organic

substances. It may be obtained, for example, by oxidizing butyric acid with nitric acid.



An interesting decomposition by which it is produced is the action of caustic potash on ethylene dicyanide, which is similar to the reaction by which propionic acid is obtained from ethyl cyanide. (Compare p. 64.)

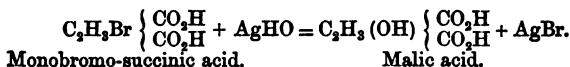


Succinic acid is a solid, crystallizing in colourless prisms. It melts at  $180^\circ$ , and is decomposed when heated to  $235^\circ$  into water and succinic anhydride,  $\text{C}_4\text{H}_4\text{O}_3$ . The alkaline salts of succinic acid are soluble in water. They give, with ferric chloride, a brown precipitate in neutral solutions. Succinic acid is dibasic, containing two atoms of the group  $\text{CO}_2\text{H}$ . Its formula may be written



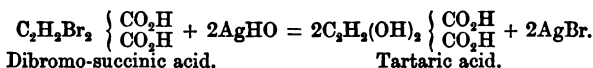
The action of bromine on succinic acid yields monobromo-succinic acid,  $\text{C}_4\text{H}_4\text{Br}_2\text{O}_4$ , and dibromo-succinic acid,  $\text{C}_4\text{H}_4\text{Br}_2\text{O}_3$ .

26. **Malic acid**,  $\text{C}_4\text{H}_6\text{O}_6$ , may be obtained by the action of silver oxide on an aqueous solution of monobromo-succinic acid—



Malic acid is contained in many fruits, and in rhubarb, &c., from which it can be easily prepared.

27. **Tartaric acid**,  $\text{C}_4\text{H}_6\text{O}_6$ , can be obtained by treating dibromo-succinic acid with silver oxide and water—



Tartaric acid exists in the juice of many fruits, and is deposited during the fermentation of wine, as *tartar*, which contains  $\text{KHC}_4\text{H}_4\text{O}_6$ .

Tartaric acid is dibasic. It forms the following potassium salts :—

Hydrogen potassium tartrate,  $\text{C}_2\text{H}_4\text{O}_2 \left\{ \begin{array}{l} \text{COKo} \\ \text{COHo} \end{array} \right.$  insoluble.  
(Cream of tartar.)

Potassium tartrate,.....  $\text{C}_2\text{H}_4\text{O}_2 \left\{ \begin{array}{l} \text{COKo} \\ \text{COKo} \end{array} \right.$  soluble.

**28. Tartar Emetic** is potassium tartrate, in which one atom of potassium is replaced by the monatomic group, Sbo. It contains  $(2\text{C}_4\text{H}_4\text{O}_6\text{KSbo})_2\text{H}_2\text{O}$ .

**29. Citric Acid** is contained, with malic acid, in the juice of the lemon and many other fruits. It contains  $\text{C}_6\text{H}_8\text{O}_7$ , and is tribasic.

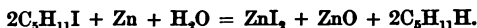
### Hydrides of the Organic Radicals.

	Boiling Point.
Methane, or methyl hydride,..... $\text{CH}_4$ ,.....	below $0^\circ\text{C}$ .
Ethane, or ethyl hydride,..... $\text{C}_2\text{H}_6$ ,.....	below $0^\circ$ .
Propane, or propyl hydride,..... $\text{C}_3\text{H}_8$ ,.....	below $0^\circ$ .
Butane, or butyl hydride,..... $\text{C}_4\text{H}_{10}$ , ...	$1^\circ$ .
Pentane, or amyl hydride,..... $\text{C}_5\text{H}_{12}$ , ...	$38^\circ$ .
Hexane, or hexyl hydride,..... $\text{C}_6\text{H}_{14}$ , ...	$69.5^\circ$ .
Heptane, or heptyl hydride,..... $\text{C}_7\text{H}_{16}$ , ...	$100.5^\circ$ .
Octane, or octyl hydride,..... $\text{C}_8\text{H}_{18}$ ,.....	$124^\circ$ .
Dodecane, or dedecetyl hydride,..... $\text{C}_{12}\text{H}_{26}$ ,...	$202^\circ$ .
Hexadecane, or hexadecetyl hydride, $\text{C}_{16}\text{H}_{34}$ , ..	$278^\circ$ .

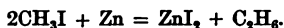
The first four of this series are gases at the ordinary temperature; those which follow are liquids of higher boiling point, the higher their molecular weight; and amongst those of the highest molecular weight are solid bodies. It is a mixture of these which is known as *paraffin*, and the series is therefore *often* called the *paraffin series*. The name denotes the persistence of these substances, which are not attacked at the ordinary temperature by sulphuric acid, nitric acid, and other powerful chemical

agents. The hydrides of this series can be prepared by the following general methods:—

(a.) By the action of zinc and water on the iodides of alcohol radicals. Thus, if amyl iodide be heated in closed tubes, together with zinc and water, to a temperature of  $150^{\circ}$  C., the following decomposition takes place—



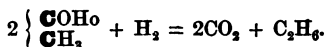
(b.) By the action of the metals alone on the alcohol iodides, *e.g.*, the action of zinc on methyl iodide yields ethyl hydride. (See p. 27.)



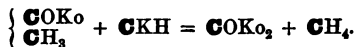
And the action of sodium on a mixture of ethyl iodide and amyl iodide gives heptyl iodide.



(c.) By electrolysis of the salts of acetic acid and its homologues. Thus potassium acetate yields at the negative pole hydrogen, and at the positive pole carbon dioxide and ethyl hydride.



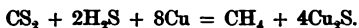
(d.) By heating together a salt of the acetic acid series with potassium, or calcium hydrate. Thus, caustic potash and potassium acetate give methyl hydride.



These hydrocarbons are also very often produced in the *destructive distillation* of organic substances. Thus, methyl hydride is one of the principal constituents of coal gas, and the coal tar contains other members of the series. Petroleum, also, which has probably been formed by some process analogous to destructive distillation, and paraffin oil consist principally of a mixture of these hydrides.

**30. Methane, Methyl Hydride, or Marsh Gas,  $CH_4$ .**—Marsh gas is so called because it is produced by the decomposition of vegetable matter in marshes. It con-

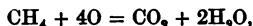
stitutes also the bulk of the gas which collects at times in coal mines, and bears the name **fire damp**. It can be synthetically built up from inorganic materials. Sulphur combines directly with carbon and with hydrogen, forming carbon disulphide and hydric sulphide. If a mixture of these substances is made to pass over red hot copper, marsh gas is obtained.



Marsh gas is prepared by heating potassium acetate (or dry sodium acetate) with soda lime—a mixture of sodium hydrate and calcium hydrate made by slacking lime in a solution of caustic soda, and then heating the mixture to drive off the excess of water. The lime is added in this case to prevent the caustic soda melting at the high temperature required, and so corroding the glass. The mixture is heated in a hard glass tube, or a hard glass flask coated with fire clay, or, best of all, in a metal retort. The gas may be collected over water in the ordinary way. The equation by which it is formed is given above.

Methane is a colourless gas, without smell, which burns in the air with a scarcely luminous flame, forming carbon dioxide and water.

The equation,



shows that the gas requires twice its own volume of oxygen for complete combustion. If the two gases are mixed in these proportions, and the mixture be set on fire, a very violent explosion occurs. If mixed with air, it also explodes, but, of course, not so violently as with pure oxygen. As two volumes of oxygen are contained in about ten volumes of air, we see that marsh gas, when exploded together with air, renders ten times its own volume of air unfit for respiration; and it is this mixture of nitrogen and carbon dioxide which, under the name of **after damp**, is often more fatal to life, in coal-mine explosions, than the fire damp itself. Marsh gas is eight times as heavy as hydrogen, and therefore ( $8 \times 0.0693 =$ )

0.5544 times as heavy as air. It is sometimes called light carburetted hydrogen, in distinction from olefiant gas, which is also called heavy carburetted hydrogen.

Marsh gas has never been reduced to a liquid. When mixed with chlorine, no action takes place in the dark; but in daylight the two gases combine, forming hydrochloric acid, and the following substitution products (already mentioned on p. 22):—

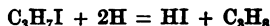
Methyl chloride, .....	$\text{CH}_3\text{Cl}$ .....	Boiling point, - 21° C.
Methylene chloride, .....	$\text{CH}_2\text{Cl}_2$ .....	„ 41°.
Chloroform, .....	$\text{CHCl}_3$ .....	„ 62°.
Carbon tetrachloride, ....	$\text{CCl}_4$ .....	„ 77°.

**31. Chloroform** is prepared on the large scale by distilling alcohol with bleaching powder. It is a colourless mobile liquid, of peculiar odour, heavier than water (sp. gr. 1.525), and insoluble in water.

By the action of nascent hydrogen on carbon tetrachloride we can replace chlorine by hydrogen, and thus pass back again through the series, finally obtaining again marsh gas.

**32. Ethyl Hydride** has been already described under the name of *methyl*.

**33. Propyl Hydride** is obtained by the action of nascent hydrogen on propyl iodide—\*



Propyl iodide is itself obtained by the action of hydriodic acid on glycerine.



Propyl hydride is a colourless gas, which burns with a bright flame, and is acted on by chlorine in daylight, forming *propyl chloride*  $\text{C}_3\text{H}_7\text{Cl}$  and other substitution products.

**34. Butyl Hydride** is identical with *ethyl*, which has been already described.

\* Strictly *isopropyl iodide*, which is isomeric with *normal propyl iodide*. For a description of these numerous isomeric modifications, the larger manuals must be consulted.

**35. Amyl Hydride** is a volatile liquid contained in American petroleum, and which can be prepared by the action of zinc and water on amyl iodide.

**36. Hexyl Hydride** is identical with *propyl*.

The remaining members of this series are of less importance.

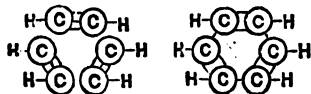
**37. Paraffin**,  $C_nH_{2n+2}$ , is a solid substance contained in several varieties of tar, and is probably a mixture of several substances of the hydride series. It was first obtained from the tar obtained in the distillation of wood, and is manufactured by the distillation of peat, and of some varieties of coal.

Paraffin is a white solid, without taste or smell, of specific gravity 0.87, and melting at about  $45^\circ$  C.

It burns with a bright flame, and is employed in the manufacture of candles and of paraffin matches.

**38. Paraffin Oil** is a mixture of liquid hydrocarbons of similar composition, obtained by the distillation of coal, &c., and resembles natural petroleum in composition and properties.

**39. Benzol**, or **Phenyl Hydride**,  $C_6H_6$ .—It has been already explained that the mode in which the carbon atoms are united in benzol is altogether peculiar. Benzol can be built up from its elements. If the current of a powerful galvanic battery be made to pass between two pieces of carbon in an atmosphere of hydrogen, the two substances unite to form the hydrocarbon *ethine* or *acetylene*,  $C_2H_2$ ; and when acetylene is strongly heated, benzol is obtained. The following equation shows how three molecules of acetylene may combine to form one molecule of benzol:—

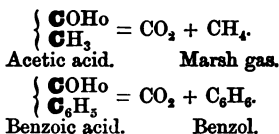


Benzol is formed in many processes of destructive distillation, and is contained in coal-tar. The lighter portion of the coal-tar oil, after treatment with sulphuric

acid, is subjected to distillation, and the portion collected which comes over while a thermometer in the retort indicates  $80^{\circ}$  to  $85^{\circ}$ . From this distillate pure benzol is obtained on freezing it in a freezing mixture, and subjecting the frozen mass to pressure.

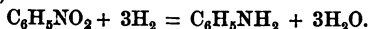
Benzol is a colourless liquid, which boils at  $81^{\circ}$ , and freezes at  $0^{\circ}$ . It is lighter than water, its specific gravity being 0.88; insoluble in water, but soluble in alcohol or ether. It is a useful solvent for resins, fats, and many other organic substances.

Pure benzol can be obtained by distilling benzoic acid with lime. A decomposition takes place precisely similar to that by which marsh gas is prepared from acetic acid, as may be seen by comparing the following equations:—



**40. Toluol,  $\text{C}_7\text{H}_8$ .**—This substance occurs together with benzol in the oil obtained from coal tar. It is the next higher homologue of benzol. Its real constitution is, however,  $\text{C}_6\text{H}_5(\text{CH}_3)$ —that is, it is methyl benzol. It can also be obtained by distilling *toluic acid*  $\left\{ \begin{array}{l} \text{COHo} \\ \text{C}_6\text{H}_4(\text{CH}_3) \end{array} \right.$  (the next higher homologue of benzoic acid) with lime, just as benzol is obtained by treating benzoic acid in the same way. Toluol boils at  $111^{\circ}$ , and does not freeze at low temperature.

**41. Aniline,  $\text{C}_6\text{H}_5(\text{NH}_2)$ ,** is now largely manufactured for the production of the aniline colours. It is obtained from benzol, which is first treated with nitric acid to convert it into **nitrobenzol**,  $\text{C}_6\text{H}_5(\text{NO}_2)$ , and this is then reduced by nascent hydrogen (by distilling it with acetic acid and iron filings)—



If the benzol contains toluol—as is always the case with

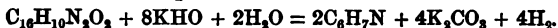
commercial benzol—the aniline obtained contains *toluidine*  $C_7H_9N$ . The production of some of the colours depends, in fact, on the presence of toluidine in the aniline employed.

Pure aniline is a colourless liquid of peculiar odour, boiling at  $182^\circ$ . It is slightly heavier than water, and nearly insoluble in it, but dissolves in alcohol and ether. It combines with acids, forming salts; thus aniline hydrochlorate contains  $C_6H_7NHCl$ . Aniline may be detected, even in very small quantity, by the red colouration produced by the action of sodium hypochlorite.

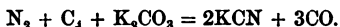
The various aniline colours are obtained by the action of oxidizing agents on aniline; thus *mauve* is obtained by oxidizing aniline with potassium bichromate.

Aniline was first obtained by distilling *indigo* with caustic potash.

**42. Indigo** is not contained ready formed in the indigo plant, but is produced by a kind of fermentation which takes place when the leaves are macerated with water, and allowed to stand. The indigo is then deposited in the form of a fine powder, which is allowed to dry, and then cut into cakes, in which condition it is sent into the market. The pure colouring matter of indigo has the formula,  $C_{16}H_{10}N_2O_2$ . It is insoluble in water and alcohol; it dissolves, however, in strong sulphuric acid, forming a dark blue solution. Nascent hydrogen acts upon indigo in a peculiar manner, converting it into a colourless and soluble substance known as **white indigo**, which contains  $C_{16}H_{12}N_2O_2$ . This fact is employed in indigo dyeing. The indigo-vat is obtained by mixing powdered indigo with a solution of ferrous sulphate and lime. The indigo is then converted into the soluble white form, and cloth dipped into this liquid, and then exposed to the air, becomes permanently dyed,—the indigo being reconverted into the insoluble form, and deposited within the fibre of the cloth. When indigo is distilled with caustic potash, aniline is obtained—

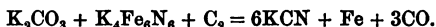


**43. Cyanic Hydride, HCN, *Hydrocyanic* or *Prussic Acid*.**  
—It has been already mentioned that, if nitrogen gas is passed over a mixture of charcoal and potassium carbonate heated to redness, potassium cyanide is formed—

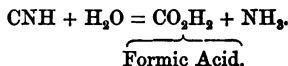


If iron be present, potassium ferrocyanide is formed, and this salt is prepared upon a somewhat large scale, by heating together scrap iron, potassium carbonate, and any refuse organic substances which contain nitrogen, such as hair, horn, or dried blood. On treating the mass with water, and evaporating, potassium ferrocyanide,  $\text{K}_4\text{FeC}_6\text{N}_6$ , separates out in large yellow crystals.

Potassium cyanide can be obtained by heating the potassium ferrocyanide with potassium carbonate and charcoal—

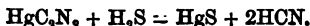


Hydrocyanic acid is given off on addition of a dilute acid to potassium cyanide, or it may be prepared by distilling potassium ferrocyanide with dilute sulphuric acid. The retort must be provided with a good condensing apparatus, the tube of which should dip into water placed in the receiver. The acid so obtained is a more or less dilute solution of the gas HCN in water. It cannot be preserved pure, as it gradually changes into ammonium formiate, a decomposition which takes place rapidly when it is boiled with an alkali—



Inversely, ammonium formiate is decomposed on heating into water and hydrocyanic acid.

In order to prepare pure hydrocyanic acid free from water, a stream of pure sulphuretted hydrogen is passed over mercuric cyanide, and the vapours led into a bent tube immersed in a freezing mixture—



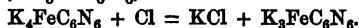
Pure hydrocyanic acid is a colourless liquid which boils at  $26.5^{\circ}$ , and freezes at  $-15^{\circ}$ . It is one of the most deadly poisons known. It is miscible with water in all proportions, and a highly dilute solution is employed in medicine. The solution of any cyanide gives, with silver nitrate, a white precipitate of silver cyanide, which is insoluble in dilute nitric acid, but soluble in solution of potassium cyanide, and in ammonia.

In order to detect hydrocyanic acid, it is best to distil the suspected liquid with tartaric acid, and to add to the distillate caustic potash, and then a mixture of ferrous and ferric salt, then, finally, hydrochloric acid. The presence of hydrocyanic acid is shown by the formation of a precipitate of Prussian blue; or the distillate may be mixed with a drop of yellow ammonium sulphide, and evaporated to dryness in a water bath; if hydrocyanic acid be present, ammonium sulphocyanide will be formed, which gives a deep red colour on addition of ferric chloride.

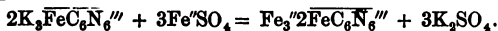
**44. Potassium Ferrocyanide,  $K_4FeC_6N_6$** , so-called yellow prussiate of potash.

In this compound the iron is present as a part of the chlorous radical, and cannot be detected by the ordinary tests for iron; the group  $FeC_6N_6$  is, therefore, tetratomic.

The solution of this salt gives, with ferric salts, a dark blue precipitate of *Prussian blue*. By passing chlorine through a solution of potassium ferrocyanide, *potassium ferricyanide*,  $K_3FeC_6N_6$ , is obtained—



In this salt, the so-called red prussiate of potash, the group  $FeC_6N_6$  is triatomic. When a solution of this salt is added to a solution of ferrous sulphate, a dark blue precipitate, known as *Turnbull's blue*, is obtained.



Turnbull's blue.

Cyanogen forms with chlorine two compounds, having the same per centage composition. The first of them is a

liquid having the formula  $\text{CNCl}$ ; it boils at  $15.5^\circ$ , and freezes at  $-5^\circ$ . Its *polymer* has the formula  $\text{C}_3\text{N}_3\text{Cl}_3$ , and is a solid, melting at  $145^\circ$ , and boiling at  $199^\circ$ .

Cyanogen forms also, with oxygen and hydrogen together, two compounds, which are polymeric, viz., cyanic acid,  $\left. \begin{smallmatrix} \text{CN} \\ \text{H} \end{smallmatrix} \right\} \text{O}$ , and cyanuric acid,  $\left. \begin{smallmatrix} \text{C}_3\text{N}_3 \\ \text{H}_3 \end{smallmatrix} \right\} \text{O}_3$ .

Cyanuric acid is obtained from urea, which may be obtained from potassium cyanide by the method described on p. 10. On heating, urea splits up into ammonia and cyanuric acid, according to the equation

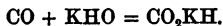


Cyanuric acid is a solid substance, and acts as a tribasic acid. If it be distilled in a retort provided with a receiver, cooled in a freezing mixture, a liquid is obtained, which is cyanic acid, the decomposition consisting in the splitting up of one molecule of cyanuric acid into three molecules of cyanic acid.

Cyanic acid is monobasic. Ammonium cyanate easily passes into the isomeric substance *urea*.

**45. Potassium Sulphocyanide,**  $\left. \begin{smallmatrix} \text{K} \\ \text{CN} \end{smallmatrix} \right\} \text{S}$  (more strictly potassium sulphocyanate), corresponds to potassium cyanate in which the oxygen has been replaced by sulphur. It is obtained by fusing potassium ferrocyanide with sulphur and potassium carbonate. Its solution gives, with the slightest trace of a ferric salt, an intense red colouration, and is thus a very delicate test for iron.

**46. Oxalylic Hydride, or Formic Acid,**  $\left\{ \begin{smallmatrix} \text{COHo} \\ \text{H} \end{smallmatrix} \right.$ —We have already seen how formic acid can be obtained from hydrocyanic acid. It can be obtained synthetically by heating together caustic potash and carbon monoxide to  $100^\circ \text{C}$ .

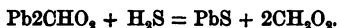


It occurs ready formed in the bodies of ants (whence its name.) It is best prepared by distilling oxalic acid to-

gether with glycerine at a temperature of about  $100^{\circ}$ ; the oxalic acid alone undergoes decomposition, splitting up into carbon dioxide and formic acid—



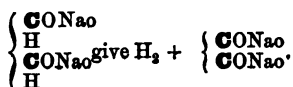
In order to obtain the anhydrous acid, lead carbonate is added to the dilute acid obtained in the above process, and the solution crystallized. The lead formiate so obtained is dried and then decomposed in a retort with dry sulphuretted hydrogen, and anhydrous formic acid distils over—



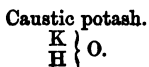
Formic acid is a colourless fluid boiling at  $100^{\circ}$ , and freezing at  $1^{\circ}$ . When heated with strong sulphuric acid it decomposes into water and carbon monoxide—



If sodium formiate be heated, hydrogen is given off, and sodium oxalate formed—



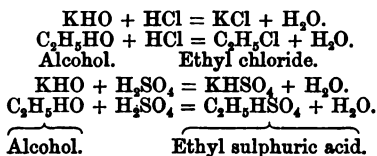
**47. The Alcohols.**—The alcohols are substances more or less resembling common alcohol, which has the formula,  $\text{C}_2\text{H}_5\text{O}$ . They correspond amongst organic substances to the hydroxides in inorganic chemistry, and may be supposed to be derived from water, by substituting an organic radical for hydrogen. Thus, both common alcohol and caustic potash may be supposed to be obtained from water by substituting for hydrogen, in the one case potassium, in the other the organic radical ethyl—



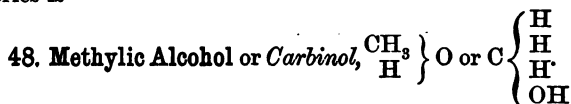
Or we may define an alcohol to be a *compound of a hydrocarbon radical with hydroxyl*. Thus, ethyl alcohol is  $\text{C}_2\text{H}_5\text{HO}$ .

The alcohols resemble the metallic hydroxides in their

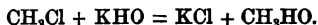
reactions with the acids, as the following equations show:—



A complete list of the alcohols of the series to which ordinary alcohol belongs is given on p. 69, together with the acids obtained from them. The first term of this series is—



This substance may be regarded as marsh gas, in which one atom of hydrogen has been replaced by hydroxyl. It is possible to obtain methyl alcohol from its elements. We have seen that marsh gas can be prepared from carbon and hydrogen, and that chlorine acts upon it in sunlight, forming methyl chloride. If methyl chloride be heated in closed tubes with caustic potash, methyl alcohol is obtained—



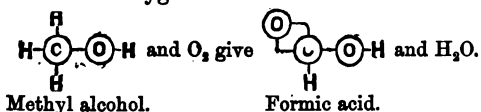
Methyl alcohol is commonly called *wood spirit*, and is obtained by the distillation of wood. The product of the distillation of wood consists of *acetic acid*, *methyl alcohol*, and a number of other substances. The mixture is saturated with lime, and distilled. The lime combines with the acetic acid, and the methyl alcohol and other substances distil over. After distilling once more over lime, dry calcium chloride is added to the distillate, which combines with the methyl alcohol, forming a solid substance, from which the other substances can be poured off, and driven off by heating to 100°, at which temperature the compound with calcium chloride is not decomposed. The dry mass is then mixed with water, and

once more distilled, when methyl alcohol distils over, and can be dried by distilling again with quick lime.

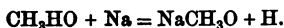
Methyl alcohol is a colourless liquid of burning taste, and smelling something like ordinary alcohol. It boils at  $66^{\circ}$ , and has a specific gravity of 0.8142; it mixes with water in all proportions. It burns like ordinary alcohol. It is employed as a substitute for alcohol, on account of its cheapness, in many manufacturing processes, and in mixture with common alcohol, as methylated spirit, which is allowed to be sold free from duty.

If methyl alcohol be acted on by oxidizing agents *formic acid* is obtained. This change may be brought about by the oxygen of the air. If a coil of platinum wire be heated to redness, and then suspended in a little beaker containing a few drops of methyl alcohol, the wire continues to glow, and formic acid and water are formed.

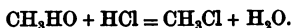
In this change, two atoms of hydrogen become replaced by one atom of oxygen.



Sodium acts violently on methyl alcohol, giving off hydrogen—

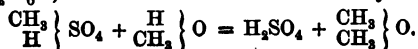


Hydrochloric acid acts on methyl alcohol, forming methyl chloride and water—



Similar compounds with bromine and iodine can be obtained.

With sulphuric acid it forms two compounds corresponding to potassium hydrogen sulphate,  $\text{KHSO}_4$ , and potassium sulphate,  $\text{K}_2\text{SO}_4$ , viz.,  $\text{CH}_3\text{HSO}_4$  and  $(\text{CH}_3)_2\text{SO}_4$ . The first of these distilled with methyl alcohol gives *methyl ether*,  $\text{C}_2\text{H}_6\text{O}$ , a substance isomeric with ethyl alcohol—

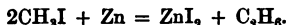


Methyl ether is a gas condensing to a liquid at  $-21^{\circ}$ .

49. Ethylic Alcohol or Methyl Carbinol,  $\left. \begin{matrix} C_2H_5 \\ H \end{matrix} \right\} O$ , or

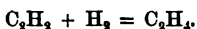
C  $\left\{ \begin{matrix} CH_3 \\ H \\ H \\ OH \end{matrix} \right.$ —Ethyl alcohol can also be obtained synthetically.

We have seen that methyl alcohol can be obtained from its elements, and from it methyl iodide can be obtained. By the action of zinc on methyl iodide, ethyl hydride is obtained—



And by the action of chlorine on this ethyl chloride  $C_2H_5Cl$  is obtained; and from this ethyl hydroxide or alcohol can be obtained.

Another method of obtaining alcohol synthetically is from acetylene, which we have seen can be produced from carbon and hydrogen. Nascent hydrogen acts on acetylene, producing ethylene—



And it has been already mentioned that alcohol can be obtained from ethylene. Alcohol is always prepared by the fermentation of sugar. Under the influence of yeast, the sugar splits up into carbon dioxide and alcohol, according to the equation

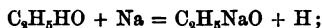


The fermentation goes on best at a particular temperature ( $25^{\circ}$  to  $30^{\circ}$ ), and with a particular concentration of the sugar solution. The fermented liquid contains dilute alcohol and other substances. By distillation the crude spirit is obtained, which contains still a considerable proportion of water, and often small quantities of other substances. One of these impurities, to be afterwards described as *amyl alcohol*, occurs especially in the spirit obtained from potatoes, and is called Fusel oil. In order to obtain alcohol free from water distillation alone is ineffective; it is necessary to employ some substance which has a great

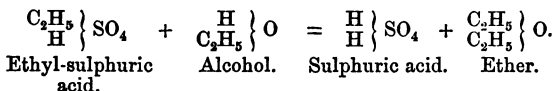
affinity for water, and quick lime is the substance commonly employed. A large retort is filled with fragments of quick lime, and the spirit poured upon the lime. The whole is allowed to stand, and then distilled in a water-bath; the product is anhydrous or absolute alcohol. Really absolute alcohol is, however, very difficult to obtain, as alcohol possesses itself a very strong affinity for water, evolving heat when mixed with water, and undergoing contraction, so that 53·7 vols. alcohol and 49·8 vols. of water produce only 100 vols. of dilute alcohol.

Pure alcohol boils at  $78\cdot4^{\circ}$ , and has never been frozen. Its specific gravity at  $0^{\circ}$  C. is 0·809. Alcohol burns with a non-luminous flame, forming carbon dioxide and water. Its vapour is 1·59 times heavier than air.

The *proof spirit* of the Excise contains 50·8 parts by weight of alcohol, and 49·2 of water, and has a specific gravity of 0·92. Brandy contains 40 to 50 per cent.; light wines, 7 or 8 per cent.; and beer, 8 to 9 per cent. Sodium reacts with ethyl alcohol, as with methyl alcohol, according to the equation

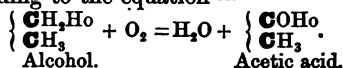


hydrochloric acid gives ethyl chloride,  $\text{C}_2\text{H}_5\text{Cl}$ ; with sulphuric acid it gives ethyl sulphate,  $\left. \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{smallmatrix} \right\} \text{SO}_4$ ; and ethyl-sulphuric acid,  $\left. \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{H} \end{smallmatrix} \right\} \text{SO}_4$ . This last substance forms salts with other metals: as potassium ethyl-sulphate,  $\text{KC}_2\text{H}_5\text{SO}_4$ ; and barium ethyl-sulphate,  $\text{Ba}_2\text{C}_2\text{H}_5\text{SO}_4$ . Ethyl-sulphuric acid decomposes alcohol, forming ether—



Oxidizing agents convert alcohol into acetic acid. A coil of platinum wire, suspended in a glass containing a few drops of strong alcohol, forms the so-called "*lamp without flame.*" Under the influence of the platinum, the

alcohol and oxygen of the air produce acetic acid and water, according to the equation—



The graphical formula of alcohol is  $\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{O}-\text{Cl}$

and it may be considered as methyl-alcohol or carbinol in which one atom of hydrogen has been replaced by methyl. Hence it is called methyl-carbinol.

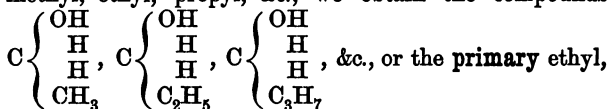
The next higher homologue of the series, *propyl alcohol*, has the formula  $\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{O}-\text{H}$ , and may be called *ethyl carbinol*, and so on through the other members of the series. *Amyl alcohol*,  $\left\{ \begin{array}{l} \text{C}_5\text{H}_{11} \\ \text{H} \end{array} \right\} \text{O}$  or  $\left\{ \begin{array}{l} \text{CH}_3\text{Ho} \\ \text{C}_4\text{H}_9 \end{array} \right\}$ , is the only other important alcohol of the series. It is the principal constituent of the Fusel oil obtained in the manufacture of potato brandy. It is a colourless liquid of disagreeable smell, boiling at  $132^\circ$ , and freezing at  $-20^\circ$ . It will be observed that in this, as in most homologous series, the boiling point rises as we pass up the series; some of the higher alcohols (as, for example, cetyl alcohol,  $\text{C}_{16}\text{H}_{33}\text{HO}$ ) are solid bodies.

**50. Secondary and Tertiary Alcohols.**—The alcohols which have been described may be supposed to be formed either on the type of water or on that of marsh gas. Methyl alcohol, for example, may be considered either as  $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{H} \end{array} \right\} \text{O}$ —that is, as water in which one atom of hydrogen

has been replaced by methyl, or as  $\text{C} \left\{ \begin{array}{l} \text{OH} \\ \text{H} \\ \text{H} \\ \text{H} \end{array} \right\}$ , that is, as

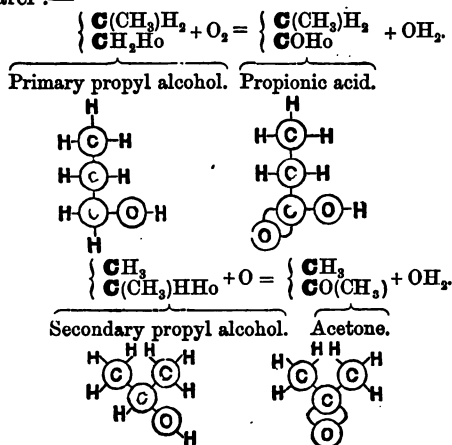
marsh gas in which one atom of hydrogen is replaced by hydroxyl, and it then receives the name of carbinol. If, then, an atom of hydrogen in carbinol be replaced by

methyl, ethyl, propyl, &c., we obtain the compounds



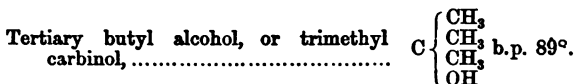
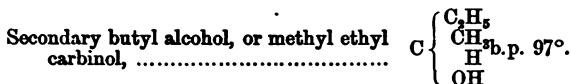
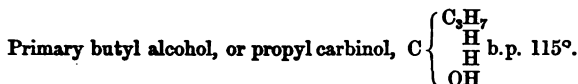
propyl, and butyl alcohols. But other substances are known which are isomeric with these propyl and butyl alcohols, but which differ in boiling point and other properties. If, for example, instead of replacing one atom of hydrogen in the original carbinol by ethyl, we replace two atoms of hydrogen, each by an atom of methyl, we obtain **secondary propyl alcohol**, which has the same composition as the primary alcohol, but possesses different properties. It boils, for example, at  $84^\circ$ , while the primary alcohol boils at  $96^\circ$ . The primary alcohol yields on oxidation, first, propionic aldehyde, and then propionic acid; but the secondary alcohol yields no aldehyde on oxidation, but instead acetone (see p. 68), and does not yield propionic acid at all.

The following graphical formulæ may make the matter clearer :—



A *primary* alcohol may then be defined as an alcohol in which the hydroxyl is attached to a carbon atom, directly united to only *one* other carbon atom. In the *secondary* alcohols, the carbon atom to which the hydroxyl is attached is united directly to *two* other carbon atoms; and in the *tertiary* alcohols this carbon atom is directly united to *three* other carbon atoms.

We know, for example, three butyl alcohols—



**51. Phenyl Alcohol or Carbolic Acid,**  $\text{C}_6\text{H}_5 \begin{matrix} \text{H} \\ \text{O} \end{matrix}$  } O.—In this substance the carbon atoms are united as in the other *aromatic compounds*.

Phenyl alcohol, or *phenol*, as it is also called, is in fact benzol in which one atom of hydrogen has been replaced by hydroxyl. It differs essentially from the true alcohols, in that it gives no acid on oxidation, and that the hydrogen of the hydroxyl is more easily displaced by metals than in the alcohols, so that this substance is as much acid as alcohol. A derivative of phenol, obtained from it by the action of nitric acid—*trinitrophenol* or *picric acid*,  $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$ —acts like a true acid, forming salts which crystallize well.

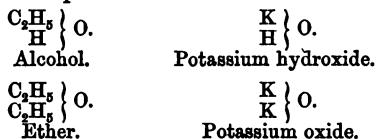
Phenol is found in the heavy oil of coal-tar, and is separated from other substances by treating the mixture with caustic soda, with which the phenol combines. The sodium phenate is decomposed by hydrochloric acid, which sets free the phenol.

Pure phenol is a white crystalline solid, melting at  $42^{\circ}$ , and boiling at  $184^{\circ}$ .

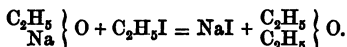
It has a peculiar smell, and burning taste, and is very poisonous. It is now largely employed as a disinfectant.

With water it forms a crystalline hydrate,  $\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_5\text{O}$ .

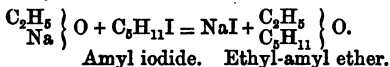
**52. The Ethers.**—We have seen that the alcohols correspond to the hydroxides amongst inorganic compounds. So the *ethers* correspond to the *oxides*—



Ether may be obtained by acting with ethyl iodide on the substance,  $\text{C}_2\text{H}_5\text{NaO}$ , obtained by the action of sodium on alcohol—



If, instead of ethyl iodide, the iodide of another alcohol radical be taken, a *mixed ether* is obtained—



**53. Ethylic Ether,  $\text{C}_4\text{H}_{10}\text{O}$ .**—Ether is commonly prepared by mixing alcohol with concentrated sulphuric acid, and heating the mixture to  $140^{\circ}\text{C}$ . Ether and water distil over, the sulphuric acid remaining behind in the retort, and acting apparently by its presence only; so that the same sulphuric acid is able to convert a comparatively large quantity of alcohol into water and ether; and, if alcohol be added as fast as it is decomposed, the process becomes continuous. In order to prepare ether by this *continuous process*, the apparatus shown in the figure may be employed. The flask contains the mixture of sulphuric acid and alcohol, and is provided with a thermometer, so that the temperature may be kept as nearly as possible constant at  $140^{\circ}$ . A continuous supply of alcohol is

kept up from the bottle, and the ether and water distil off and collect in the bottle in two layers, the lower of which is water, and the upper ether, containing alcohol and

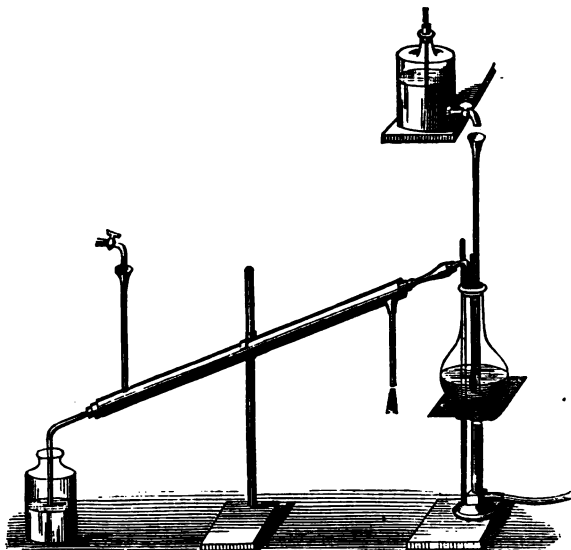
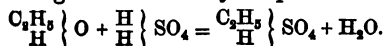


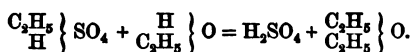
Fig. 4.

some other impurities. To purify it it is shaken with dilute caustic soda, then decanted off, and some sticks of solid caustic potash put into it; then, after standing some time, it is poured off, and distilled in a water-bath.

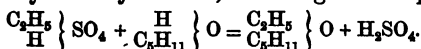
The reactions which take place in this process are the following:—The sulphuric acid first reacts with the alcohol, forming water and ethyl-sulphuric acid—



*And this ethyl-sulphuric acid then decomposes more alcohol, forming ether, and reproducing sulphuric acid—*



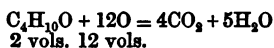
That this is what takes place, and that the ether is not formed by simple abstraction of water from the alcohol, may be seen from the following experiment:—If, in the continuous process, the mixture of ethyl alcohol and sulphuric acid be supplied, not with ethyl alcohol, but with amyl alcohol, the mixed ether,  $\text{C}_2\text{H}_5 \left\{ \begin{smallmatrix} \text{H} \\ \text{C}_5\text{H}_{11} \end{smallmatrix} \right\} \text{O}$ , is obtained, and not a mixture of the two ethers,  $\text{C}_2\text{H}_5 \left\{ \begin{smallmatrix} \text{H} \\ \text{C}_2\text{H}_5 \end{smallmatrix} \right\} \text{O}$  and  $\text{C}_5\text{H}_{11} \left\{ \begin{smallmatrix} \text{H} \\ \text{C}_5\text{H}_{11} \end{smallmatrix} \right\} \text{O}$ ; the ethyl-sulphuric acid, first formed, being decomposed by the amyl alcohol, according to the equation—



Pure ether is a colourless, very mobile liquid, having a peculiar smell and burning taste. It boils at  $34.5^\circ$ . It is insoluble in water, and lighter than that liquid, having a specific gravity of 0.736.

Ether is very inflammable, and should always be distilled by means of hot water only. It burns with a bright flame, forming of course carbon dioxide and water. Mixed with oxygen, it forms a violently explosive mixture.

The equation

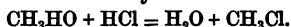


shows that it requires six times its own volume of oxygen for complete combustion.

The molecular weight of ether being 74, it follows that its vapour is 37 times as heavy as the same volume of hydrogen; and its specific gravity, in reference to air as unity, is  $37 \times 0.0693$ , or 2.564. The vapour can be poured from one vessel to another, like carbon dioxide.

**54. Haloid Ethers** is the name given to the compounds of ethyl and the other alcohol radicals with the negative or chlorous elements; as, for example, ethyl chloride,  $\text{C}_2\text{H}_5\text{Cl}$ , amyl iodide,  $\text{C}_5\text{H}_{11}\text{I}$ , &c.

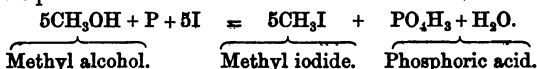
**55. Methyl Chloride**,  $\text{CH}_3\text{Cl}$ , is obtained by the action of hydrochloric acid on methyl alcohol—



It is a colourless gas, of pleasant ethereal smell, which condenses to a liquid at  $-21^\circ$ .

**56. Methyl Bromide**,  $\text{CH}_3\text{Br}$ , is obtained by the action of bromine and phosphorus on methyl alcohol. It is a colourless liquid, which boils at  $13^\circ$ .

**57. Methyl Iodide**,  $\text{CH}_3\text{I}$ , is obtained by the action of iodine and phosphorus on methyl alcohol, according to the equation—



It is a colourless liquid, of specific gravity 2.2, and boiling at  $43^\circ$ .

**58. Methyl Cyanide**(so-called),  $\left\{ \begin{array}{c} \text{CH}_3 \\ \text{CN} \end{array} \right.$ , is obtained by distilling together potassium cyanide and potassium methyl sulphate—



It is a liquid which boils at  $77^\circ$ . When heated with caustic potash it undergoes a decomposition which is interesting, as it enables us to pass from the methyl series to the ethyl series; the cyanide yields *potassium acetate* and ammonia—



We infer from this decomposition that the two carbon atoms in this substance are directly united together, and not each united with the nitrogen atom, in fact, that its

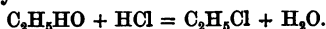
formula is  $\text{N} \equiv \underset{\text{H}}{\underset{|}{\text{C}}} - \underset{\text{H}}{\underset{|}{\text{C}}} - \text{H}$ , and not  $\text{C} \equiv \text{N} - \underset{\text{H}}{\underset{|}{\text{C}}} - \text{H}$ . Indeed,

the substance which has this last formula is also known. It is the true methyl cyanide, and boils at  $58^\circ$ . It is not

\* To indicate its connection with acetic acid this substance has been called *acetonitrile*. See p. 87.

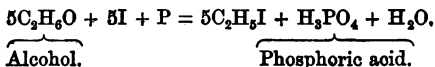
decomposed by caustic potash in the manner shown above, but is decomposed by acids into formic acid and  $\text{CH}_3\text{NH}_2$ —the two carbon atoms thus separating from each other.

59. **Ethyl Chloride**,  $\text{C}_2\text{H}_5\text{Cl}$ , is prepared by saturating alcohol with hydrochloric acid, and then heating the solution in a flask. The gas which comes off is washed through warm water, passed over calcium chloride to dry it, and then into a tube cooled in a freezing mixture, when the ethyl chloride condenses as a colourless liquid—



Ethyl chloride is a colourless pleasant smelling liquid which is very volatile, boiling at  $12.5^\circ$ . Its vapour burns with a flame tinged with green.

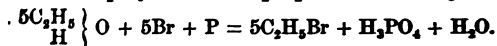
60. **Ethyl Iodide**,  $\text{C}_2\text{H}_5\text{I}$ , is prepared by the action of iodine and phosphorus on alcohol, according to the equation—



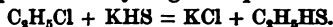
50 grams phosphorus are placed in a retort provided with a good condensing arrangement, and having a glass globe, with a tube and tap, fitted into the tubulature. 700 grams alcohol are poured on to 1000 grams iodine in a beaker, and the solution obtained poured into the globe. The retort is then heated in a water bath till the phosphorus melts, and the solution of iodine is then allowed to flow slowly into the retort. The distillate first obtained consists of alcohol containing ethyl iodide in solution. It is poured back on to the iodine remaining undissolved in the beaker, which it dissolves more freely than the alcohol alone, and the solution of iodine so obtained introduced again into the retort. When all the iodine has been used up, the ethyl iodide obtained is washed with water and redistilled.

Ethyl iodide is a colourless heavy liquid, boiling at  $72^\circ$ . It is employed in the preparation of very many other ethyl compounds. It becomes brown coloured by the *action of light*, owing to the separation of iodine.

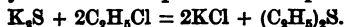
**61. Ethyl Bromide**,  $C_2H_5Br$ , is obtained by a process similar to that employed for the preparation of ethyl iodide.



Ethyl forms, with sulphur, two compounds corresponding to alcohol and ether. The first of these, called *mercaptan*,  $C_2H_5HS$ , is obtained by the action of ethyl chloride on potassium hydrogen sulphide.



It is a colourless liquid, with an intensely disagreeable smell; it boils at  $36^\circ$ , and burns in air with a blue flame. *Ethyl sulphide*,  $(C_2H_5)_2S$ , corresponding to ether in which oxygen has been replaced by sulphur, is obtained by the action of ethyl chloride on potassium sulphide—



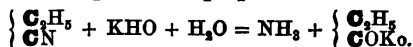
Ethyl sulphide has the same disagreeable smell as mercaptan; it boils at  $91^\circ$ .

**62. Ethyl Cyanide**,  $\begin{matrix} CH_2(CH_3) \\ | \\ CN \end{matrix}$ .—There are two substances of the formula  $C_3H_5N$ , as there are two isomeric methyl cyanides.

The substance having the formula given above (in which the carbon atoms are directly united together) is obtained by distilling a mixture of potassium cyanide and potassium ethyl sulphate—



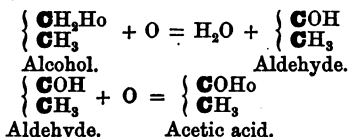
It boils at  $97^\circ$ , and is decomposed by caustic potash into ammonia and potassium propionate—\*



This decomposition enables us to pass from the two-carbon compounds to the three-carbon compounds. The isomer which is not so decomposed boils at  $77^\circ$ , and has the formula  $\begin{matrix} C_2H_5 \\ | \\ NC \end{matrix}$ .

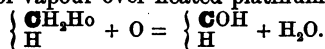
\* Hence this substance is called *propionitrile*.

**63. The Aldehydes.**—We have seen that oxidizing agents convert methyl alcohol into formic acid, and ethyl alcohol into acetic acid. In like manner each of the alcohols yields an acid by oxidation. It is found, however, that the oxidation of an alcohol takes place in two successive steps, and the intermediate substance is called an *aldehyde*. Thus, if alcohol be treated with chromic acid, or with a mixture of potassium bichromate and sulphuric acid, it is oxidized to aldehyde, which easily oxidizes further to acetic acid—

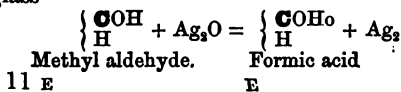


An aldehyde is thus a compound of hydrogen or alcohol radical with the group  $\text{COH}$ . We shall see presently that an acid contains the group  $\text{COHo}$ , and we have already seen that an alcohol contains the group  $\text{CH}_2\text{Ho}$ . The aldehydes very easily take up oxygen and become acids, the group  $\text{COH}$  being oxidized to  $\text{COHo}$ ; and less easily, by the action of nascent hydrogen, the group  $\text{COH}$  of the aldehyde is reduced to  $\text{CH}_2\text{Ho}$ , the aldehyde being converted into the alcohol, the methyl or other alcohol radical remaining unaltered.

**64. Formic Aldehyde,**  $\left\{ \begin{array}{l} \text{COH} \\ \text{H} \end{array} \right\}$ , is a colourless gas, which has an irritating smell. It is formed by passing air and methyl alcohol vapour over heated platinum—

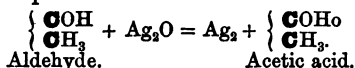


It has a great affinity for oxygen. A solution of methyl aldehyde in methyl alcohol, mixed with an ammoniacal solution of silver nitrate, and gently warmed, reduces the silver to the metallic state, forming a brilliant mirror on the glass—



**65. Acetic Aldehyde,**  $\left\{ \begin{smallmatrix} \text{COH} \\ \text{C}_2\text{H}_3 \end{smallmatrix} \right.$ , is formed by the action of oxidizing agents on alcohol, such as chromic acid, or a mixture of sulphuric acid and manganese dioxide, or by leading alcohol and oxygen over platinum. The best method of preparing aldehyde is to oxidize alcohol by means of a mixture of sulphuric acid and potassium bichromate, and to pass the gas evolved into ether which absorbs the aldehyde vapour. Ammonia gas is then led into this solution, when a compound of aldehyde and ammonia separates out in crystals. This substance contains  $\text{C}_2\text{H}_4\text{ONH}_3$ ; and by distillation with dilute sulphuric acid it yields pure aldehyde. Aldehyde is a colourless liquid, boiling at  $21^\circ$ , and possessing a suffocating smell.

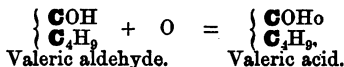
If warmed with an ammoniacal solution of silver nitrate, the silver is deposited as a brilliant metallic mirror—



Aldehyde unites with nascent hydrogen, forming alcohol.

**66. Valeric Aldehyde,**  $\left\{ \begin{smallmatrix} \text{COH} \\ \text{C}_4\text{H}_9 \end{smallmatrix} \right.$ , is obtained by oxidizing amyl alcohol with a mixture of sulphuric acid and potassium bichromate.

It is a liquid which boils at  $98^\circ$ . It is reduced by nascent hydrogen to amyl alcohol, and by oxygen it is easily converted into valeric acid—



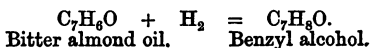
**67. Benzoic Aldehyde or Oil of Bitter Almonds,**  $\left\{ \begin{smallmatrix} \text{COH} \\ \text{C}_6\text{H}_5 \end{smallmatrix} \right.$ , is obtained by bruising bitter almonds with water, and distilling. It does not exist ready formed in the almonds, but is produced by a peculiar fermentation which takes place. The almonds contain a substance called amygdalin,  $\text{C}_{20}\text{H}_{27}\text{NO}_{11}$ , which, under the action of a peculiar

ferment, also contained in the almonds, splits up into grape sugar, bitter almond oil, and hydrocyanic acid—

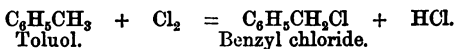


The almonds are first crushed and pressed to remove the fixed oil they contain, and the pulp is mixed with water and allowed to stand for a day. It is then subjected to distillation, when the bitter almond oil distils over.

Oil of bitter almonds is the aldehyde containing the radical phenyl, instead of a radical of the regular alcohol series—the phenyl being constituted as in the other aromatic compounds. It is a colourless liquid, having a peculiar smell, and boiling at  $180^\circ$ . It is employed in cookery as a flavour, a use which is dangerous, as the oil always contains an admixture of hydrocyanic acid. Benzoic aldehyde is converted by oxidation into benzoic acid; and by nascent hydrogen (by mixing it with water and sodium amalgam) into *benzyl alcohol*,  $\left\{ \begin{array}{l} \text{C}_6\text{H}_5\text{O} \\ \text{C}_6\text{H}_5 \end{array} \right.$ —



Benzyl alcohol may also be obtained from benzyl chloride, which is obtained by the action of chlorine on toluol—



Benzyl alcohol is a colourless liquid, boiling at  $207^\circ$ . When gently oxidized, it yields benzoic aldehyde; and, when oxidized more strongly, as by chromic acid, it yields benzoic acid.

68. Salicyl Aldehyde,  $\left\{ \begin{array}{l} \text{COH} \\ \text{C}_6\text{H}_4\text{H}_0 \end{array} \right.$  or  $\text{C}_7\text{H}_6\text{O}_2$ , is the starting point of the salicyl group of compounds. It differs from benzoic aldehyde simply in containing an atom of hydroxyl instead of an atom of hydrogen. It is a volatile oil, which may be extracted from the flowers of the meadow sweet, which owe their fragrance to this sub-

stance. It may also be obtained from salicin, a bitter substance obtained from willow bark. Salicyl aldehyde boils at  $182^{\circ}$ . By oxidation it forms salicylic acid,  $C_7H_6O_3$ .

69. Salicylic Acid,  $\left\{ \begin{array}{l} \text{COHo} \\ C_6H_4Ho \end{array} \right.$ , occurs also in the oil of winter green, as methyl salicylate,  $CH_3C_7H_5O_3$ .

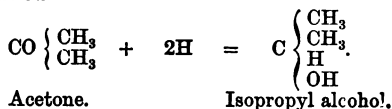
70. Acetone,  $C_3H_6O$ , is a colourless, pleasant-smelling liquid which boils at  $56^{\circ}$ . It is obtained by the distillation of calcium acetate, and occurs, together with methyl alcohol and acetic acid, in the products of the distillation of wood.

Acetone is the best known of the class of bodies called *ketones*. A ketone is a compound of carbon monoxide with two alcohol radicals—acetone itself being  $CO \left\{ \begin{array}{l} CH_3 \\ CH_3 \end{array} \right.$ ; or they may be supposed to be obtained from aldehyde by replacing one atom of hydrogen by an alcohol radical.

Other ketones have the formulæ—

$CO \left\{ \begin{array}{l} CH_3 \\ C_2H_5 \end{array} \right.$	.....	Boiling point, $81^{\circ}$ .
$CO \left\{ \begin{array}{l} CH_3 \\ C_3H_7 \end{array} \right.$	.....	„ „ $101^{\circ}$ .
$CO \left\{ \begin{array}{l} C_2H_5 \\ C_2H_5 \end{array} \right.$	.....	„ „ $101^{\circ}$ .
$CO \left\{ \begin{array}{l} CH_3 \\ C_4H_9 \end{array} \right.$	.....	„ „ $120^{\circ}$ .
$CO \left\{ \begin{array}{l} C_2H_5 \\ C_3H_7 \end{array} \right.$	.....	„ „ $128^{\circ}$ .
$CO \left\{ \begin{array}{l} C_3H_7 \\ C_3H_7 \end{array} \right.$	.....	„ „ $144^{\circ}$ .

Acetone, when acted on by nascent hydrogen, yields secondary propyl alcohol, or isopropyl alcohol, as it is sometimes called—

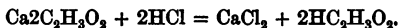


71. The Acids.—The following is a complete list of the alcohols homologous with methyl alcohol, and the acids which are obtained from them, so far as they are known:—

ALCOHOLS.				ACIDS.			
Name.	Formula.	Boiling Point.	Melting Point.	Name.	Formula.	Boiling Point.	Melting Point.
Methyl Alcohol,	$\text{CH}_3\text{O}$	66° C.	—	Formic Acid,	$\text{CH}_2\text{O}_2$	100°	1°
Ethyl "	$\text{C}_2\text{H}_5\text{O}$	78.4°	—	Acetic "	$\text{C}_2\text{H}_4\text{O}_2$	118°	17°
Propyl "	$\text{C}_3\text{H}_7\text{O}$	97°	—	Propionic "	$\text{C}_3\text{H}_6\text{O}_2$	140°	—
Butyl "	$\text{C}_4\text{H}_9\text{O}$	115°	—	Butyric "	$\text{C}_4\text{H}_8\text{O}_2$	162°	—
Amyl "	$\text{C}_5\text{H}_{11}\text{O}$	132°	—	Valeric "	$\text{C}_5\text{H}_{10}\text{O}_2$	175°	—
Hexyl "	$\text{C}_6\text{H}_{13}\text{O}$	150°	—	Caproic "	$\text{C}_6\text{H}_{12}\text{O}_2$	199°	5°
Heptyl "	$\text{C}_7\text{H}_{15}\text{O}$	170°	—	Heptanthylic "	$\text{C}_7\text{H}_{14}\text{O}_2$	219°	—
Octyl "	$\text{C}_8\text{H}_{17}\text{O}$	190°	—	Caprylic "	$\text{C}_8\text{H}_{16}\text{O}_2$	236°	14°
Nonyl "	$\text{C}_9\text{H}_{19}\text{O}$	—	—	Pelargonic "	$\text{C}_9\text{H}_{18}\text{O}_2$	260°	18°
Decetyl "	$\text{C}_{10}\text{H}_{21}\text{O}$	212°	—	Rutic "	$\text{C}_{10}\text{H}_{20}\text{O}_2$	270°	30°
—	—	—	—	Lauric "	$\text{C}_{12}\text{H}_{24}\text{O}_2$	—	43.6°
—	—	—	—	Myristic "	$\text{C}_{14}\text{H}_{28}\text{O}_2$	—	53.8°
Cetyl "	$\text{C}_{16}\text{H}_{33}\text{O}$	—	50°	Palmitic "	$\text{C}_{16}\text{H}_{32}\text{O}_2$	—	62°
				Margaric "	$\text{C}_{17}\text{H}_{34}\text{O}_2$	—	—
				Stearic "	$\text{C}_{18}\text{H}_{36}\text{O}_2$	—	69.2°
				Arachic "	$\text{C}_{20}\text{H}_{40}\text{O}_2$	—	75°
				Behenic "	$\text{C}_{22}\text{H}_{44}\text{O}_2$	—	76°
				Hyenic "	$\text{C}_{25}\text{H}_{50}\text{O}_2$	—	77°
Ceryl "	$\text{C}_{27}\text{H}_{56}\text{O}$	—	79°	Cerotic "	$\text{C}_{26}\text{H}_{52}\text{O}_2$	—	78°
Myricyl "	$\text{C}_{30}\text{H}_{62}\text{O}$	—	83°	Melissic "	$\text{C}_{30}\text{H}_{60}\text{O}_2$	—	80°

The organic acids, like the inorganic, differ in basic power. Nitric acid forms only one salt with a monatomic metal such as potassium, and is therefore *monobasic*. Sulphuric acid forms the two salts,  $K_2SO_4$ , and  $KHSO_4$ , and is therefore *dibasic*; while phosphoric acid is *tribasic*, forming the three salts,  $K_3PO_4$ ,  $K_2HPO_4$ , and  $KH_2PO_4$ . In the same way acetic acid is monobasic, forming only  $KC_2H_3O_2$ . Oxalic acid is dibasic, forming the salts,  $K_2C_2O_4$ , and  $KHC_2O_4$ ; while citric acid,  $C_6H_8O_7$ , forms the three salts,  $K_3C_6H_5O_7$ ,  $K_2HC_6H_5O_7$ , and  $KH_2C_6H_5O_7$ , and is therefore tribasic. It is found that the basic power of an inorganic acid is determined by the number of times it contains the group oxatyl,  $CO_2H$ . Thus acetic acid, which is monobasic, contains it only once,  $\begin{Bmatrix} CH_3 \\ COHO \end{Bmatrix}$ . Oxalic acid contains it twice,  $\begin{Bmatrix} COHO \\ COHO \end{Bmatrix}$  and is dibasic; while citric acid contains it three times.

**72. Acetic Acid,**  $\begin{Bmatrix} CH_3 \\ COHO \end{Bmatrix}$  is obtained by the oxidation of alcohol, and, as already mentioned, in the destructive distillation of wood. In this last method the wood is distilled at a red heat in iron retorts. The liquid which distils over is poured off from the tar and redistilled. The first portions which come over constitute wood-naphtha, then the acetic acid distils over. In order to separate it from the tarry matters with which it is mixed, it is neutralized by lime, which combines with the acetic acid, forming calcium acetate. The tar rises to the surface of the liquid, and is skimmed off while the solution is evaporated to dryness. The dry residue, containing calcium acetate, is gently roasted to get rid of impurities, and is then decomposed with hydrochloric acid, when acetic acid distils over—



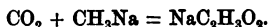
Alcohol is converted into acetic acid by most oxidizing agents, and by the oxygen of the air in presence of finely divided platinum, or of certain ferments, which induce the acetic fermentation. If wine or any alcoholic liquid

be mixed with some vinegar and yeast, and kept in loosely closed vessels at a temperature of about  $25^{\circ}$ , the alcohol is gradually converted into vinegar or acetic acid. Or the change may be brought about more quickly, by allowing the alcoholic liquid to trickle slowly down a sort of stack or wall formed of loose wood shavings, saturated with vinegar, through which the air blows freely.

In order to obtain pure acetic acid, strong vinegar is saturated with sodium carbonate and evaporated to dryness. The sodium acetate so obtained is distilled in a retort with concentrated sulphuric acid.

Pure acetic acid is a colourless liquid, which smells and tastes strongly acid, and which boils at  $118^{\circ}$ , and (if free from water) freezes at  $17^{\circ}$ . It mixes with water in every proportion.

We have seen that an acetate is formed by the action of caustic potash on acetonitrile, or methyl cyanide. Another method by which an acetate can be obtained from the methyl series is by the action of carbon dioxide on a compound which methyl forms with sodium, and which contains  $\text{CH}_3\text{Na}$ , according to the following equation—



Several methods are known by which we can obtain the alcohol from the acid; for example, ordinary alcohol from acetic acid. It is thus possible to obtain ethyl compounds from methyl compounds, and by similar processes to obtain propyl compounds from ethyl compounds, and so to pass up the series.

The most important salts of acetic acid are the following:—

*Potassium acetate*,  $\text{KC}_2\text{H}_3\text{O}_2$ , crystallizes with difficulty, and is deliquescent.

*Sodium acetate*,  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$ , crystallizes easily.

*Aluminium acetate* and *ferric acetate* are used as mordants in dyeing.

*Lead acetate*,  $\text{PbC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$  (sugar of lead), is pre-

pared by dissolving lead oxide in dilute acetic acid and crystallizing. It is easily soluble in water.

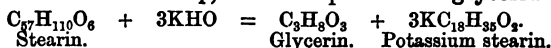
*Propionic acid*,  $\left\{ \begin{array}{l} \text{COH} \\ \text{C}_2\text{H}_5 \end{array} \right.$  Potassium propionate, as already mentioned, is obtained by the action of caustic potash on propionitrile or ethyl cyanide. By distilling it with sulphuric acid, propionic acid is easily obtained.

*Butyric acid*,  $\left\{ \begin{array}{l} \text{COH} \\ \text{C}_3\text{H}_7 \end{array} \right.$ , is produced when sugar undergoes a peculiar kind of fermentation, called the butyric fermentation.

*Valerianic acid*,  $\left\{ \begin{array}{l} \text{COH} \\ \text{C}_4\text{H}_9 \end{array} \right.$ , occurs in the root of the valerian plant. It can also be obtained by oxidizing amyl alcohol.

The remainder of the acids of this series are of little importance, until we come to the higher members of the series, those, namely, which are contained in fats. It is from them that the whole series receives the name—

**73. Fatty Acid Series.**—The principal ones are palmitic and stearic acids, which are contained in various proportions in several common fats and oils, such as suet, lard, olive oil, palm oil, spermaceti, &c. If we take mutton-suet, for example, and heat it with about ten times its volume of ether, we obtain a solution which, on cooling, deposits pearly scales of a substance called **stearin**. The ether retains, in solution, two somewhat similar substances, called **olein** and **palmitin**. The stearin so obtained contains  $\text{C}_{57}\text{H}_{110}\text{O}_6$ . If it be mixed with solution of caustic potash, and the solution be heated, best by blowing steam into it, the stearin is decomposed with the formation of a **soap**, and the separation of **glycerin**—

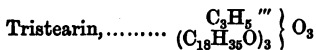
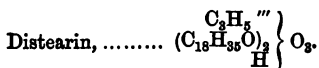
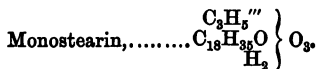


The potassium stearate, which is a soap, can be separated by saturating the solution with common salt, when the soap forms a cake on the surface of the liquid. In the same way, each of the fats is decomposed by this

process, which is termed saponification, into *glycerin*, and the alkaline salt of a *fatty acid*. If the potassium stearate be then decomposed by adding hydrochloric acid to its hot solution, the stearic acid is separated, and forms a layer on the top.

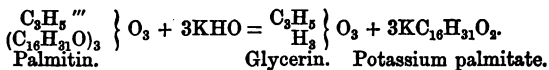
**74. Stearic Acid,**  $\left\{ \begin{array}{c} \text{C}^{\text{O}}\text{H}^{\text{O}} \\ \text{C}_{17}\text{H}_{35} \end{array} \right\} \text{O}$ , is a white solid substance, which crystallizes from its solution in ether in pearly plates. It is insoluble in water. It melts at  $70^{\circ}$  C. It is now prepared on a somewhat large scale, to be used in making the so-called stearin candles. It forms salts, most of which are insoluble in water; but the alkaline stearates are soluble. Sodium stearate constitutes the bulk of ordinary hard soaps.

Stearic acid and glycerin form three different compounds termed **stearins**. They are as follows:—



It is tristearin which constitutes the bulk of mutton suet.

**75. Palmitic Acid,**  $\left\{ \begin{array}{c} \text{C}^{\text{O}}\text{H}^{\text{O}} \\ \text{C}_{15}\text{H}_{31} \end{array} \right\} \text{O}$ , is contained in *palm oil* and in *spermaceti*. It may be obtained from palm oil by saponification, when the oil yields glycerin, and the alkaline palmitate.



The constitution of spermaceti is peculiar. It is not a derivative of glycerin at all, but is the palmitate de-

rived from cetyl alcohol or cetyl palmitate, containing

$$\left. \begin{array}{l} \text{C}_{18}\text{H}_{31}\text{O} \\ \text{C}_{16}\text{H}_{33} \end{array} \right\} \text{O}.$$

**76. Oleic Acid,**  $\text{C}_{18}\text{H}_{33}\text{O} \left\{ \begin{array}{l} \text{O} \\ \text{H} \end{array} \right\}$ , does not belong to the fatty acid series, but to a closely related series. It forms, with glycerin, a fat called olein,  $\text{C}_{57}\text{H}_{104}\text{O}_6$ , which is a liquid, and constitutes the bulk of olive and many other oils.

**77. Glycerin,**  $\text{C}_3\text{H}_5 \left\{ \begin{array}{l} \text{HO} \\ \text{HO} \\ \text{HO} \end{array} \right\}$ , is obtained, as we have seen,

by the saponification of many natural fats. It is largely obtained as a by-product in the manufacture of soap. It was originally obtained in the preparation of the common lead-plaster, by decomposing olive oil with lead-oxide. The insoluble lead-soap was precipitated, and the glycerin remained in solution. Pure glycerin is now obtained by decomposing fats with super-heated steam. The fats at the high temperature employed react with water, splitting up into glycerin and the fatty acids which distil over together with water, and separate into two layers in the receiver.

Glycerin is a colourless viscid liquid of specific gravity 1.27, of an intensely sweet taste. It is soluble in water in all proportions. It cannot be obtained solid, nor can it be distilled without decomposition. In presence of water-vapour, however, it distils tolerably easily. Dilute nitric acid oxidizes glycerin, with formation of the acid termed *glyceric acid*. Concentrated nitric acid converts glycerin into the terribly explosive nitroglycerin,  $\text{C}_3\text{H}_5(\text{NO}_2)_3\text{O}_3$ , the so-called glonoin, employed for blasting purposes.

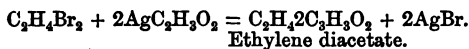
Glycerin is a triatomic alcohol—that is, instead of being derived like ordinary alcohol, from one molecule of water by the replacement of one atom of hydrogen by a monatomic radical, it is derived from three molecules of water by replacing three atoms of hydrogen by the triatomic radical  $\text{C}_3\text{H}_5$ ; or it may be considered as a compound of  $\text{C}_3\text{H}_5$  with three molecules of hydroxyl.

It may be well to place together the formulæ of some monatomic, diatomic, and triatomic alcohols—

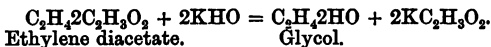
Monatomic.	Diatomic.	Triatomic.
$C_2H_5'Ho$ , b.p. 78°.	$C_2H_4''Ho_2$ , b.p. 197°.	
Ethyl alcohol.	Glycol.	
$C_3H_7'Ho$ , b.p. 96°.	$C_3H_6''Ho_2$ , b.p. 188°.	$C_3H_5'''Ho_3$ .
Propyl alcohol.	Propene glycol.	Glycerin.
$C_4H_9'Ho$ , b.p. 109°.	$C_4H_8''Ho_2$ , b.p. 183°.	
Butyl alcohol.	Butylene glycol.	
$C_5H_{11}'Ho$ , b.p. 132°.	$C_5H_{10}''Ho_2$ , b.p. 177°.	$C_5H_9'''Ho_3$ .
Amyl alcohol.	Amylene glycol.	Amyl glycerin.

It will be noticed that while the boiling point increases as we pass up the monatomic alcohol series, it decreases in the glycol series, which thus forms an exception to the ordinary rule.

78. Glycol,  $C_2H_4Ho_2$ , is obtained from ethylene by forming first the dibromide, and then acting on this with silver acetate—



The *ethylene diacetate* is then decomposed by caustic potash—



Glycol is a colourless thick liquid, of specific gravity 1.125. It is soluble in water. When oxidized by means of spongy platinum it yields *glycollic acid*, and when further oxidized—for example, by hot nitric acid—it yields *oxalic acid*—



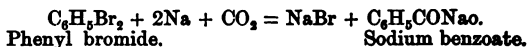
79. Benzoic Acid,  $\begin{Bmatrix} COHo \\ C_6H_5 \end{Bmatrix}$ , does not belong to the fatty acid series, but to the aromatic compounds.

It occurs in many resins, particularly in *gum benzoin*, from which it can be obtained by simple sublimation. The gum benzoin is placed in a shallow iron dish, which is covered with paper in which holes have been pierced,

and which acts as a sort of filter. Over this is placed a cone of paper which acts as a receiver. On heating the iron dish in a sand bath the benzoic acid volatilizes, and forms shining needle-shaped crystals inside the paper cone.

Benzoic acid is also obtained by the oxidation of bitter almond oil. It also results from the oxidation of many other aromatic substances, such as benzyl alcohol, toluol, &c.

Benzoic acid is produced by the simultaneous action of sodium and carbon dioxide on phenyl bromide—



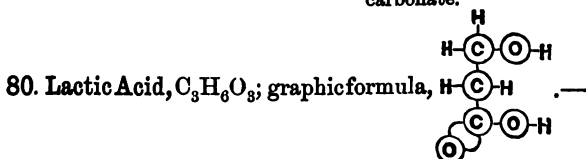
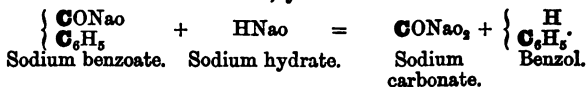
A reaction which may be compared with the production of sodium acetate by the action of carbon dioxide, on  $\text{CH}_3\text{Na}$ , already mentioned. Phenyl cyanide is decomposed by caustic potash yielding benzoic acid, just as methyl cyanide yields acetic acid—



Benzoic acid crystallizes in long flexible needles of a glittering white. It melts at  $120^\circ$ , and boils at  $250^\circ$ . It is only slightly soluble in cold water; more easily in hot water, and in alcohol.

Benzoic acid is monobasic; its salts are mostly soluble in water. With ferric chloride they give a red precipitate of ferric benzoate.

As already mentioned, sodium benzoate, distilled with caustic soda or with lime, yields benzol—



Ordinary alcohol is derived from the saturated hydrocarbon,  $C_2H_6$ , by the replacement of one atom of hydrogen by hydroxyl, giving  $C_2H_5Ho$ . There exists, however, a compound—a sort of alcohol—called *glycol*, which is derived from  $C_2H_6$  by replacing two atoms of hydrogen by  $Ho$ —having, therefore, the formula,  $C_2H_4Ho_2$ .

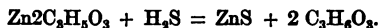
Ordinary alcohol, by oxidation, gives only one acid—acetic acid—which is monobasic. Glycol, on the other hand, gives, by oxidation, two acids—one monobasic, called *glycollic acid*; and the other dibasic, which is *oxalic acid*.

In like manner, from the saturated hydrocarbon,  $C_3H_8$ , is derived a glycol called *propylene glycol*, which, by oxidation, yields two acids, and the first of these—the monobasic one—is *lactic acid*. These relationships may be seen from the following table, which should be carefully studied :—

Alcohols.	Monobasic Acids.	Dibasic Acids.
$\begin{cases} CH_3Ho \\ CH_2Ho \end{cases}$ Glycol.	$\begin{cases} CH_3Ho \\ COHo \end{cases}$ Glycollic acid.	$\begin{cases} COHo \\ COHo \end{cases}$ Oxalic acid.
$\begin{cases} CH_3Ho \\ CH_2 \\ CH_2Ho \end{cases}$ Propylene glycol.	$\begin{cases} CH_3Ho \\ CH_2 \\ COHo \end{cases}$ Lactic acid.	$\begin{cases} COHo \\ CH_2 \\ COHo \end{cases}$ Malonic acid.

Lactic acid is contained in sour milk. It is formed from sugar by a particular kind of fermentation. The method of preparing it is as follows:—Three kilogrammes of sugar and 15 grs. tartaric acid are dissolved in 17 litres of boiling water, and, after standing some days, a mixture of 100 grs. of decayed cheese in 4 litres of sour milk is added, together with 1200 grs. zinc oxide, and the whole is allowed to stand for eight or ten days at a temperature of  $40^\circ$  to  $45^\circ$ . The lactic acid formed dissolves the zinc oxide, forming zinc lactate. When the mixture has stood long enough it is heated to boiling and filtered, and the filtrate evaporated, when zinc

lactate crystallizes out. It is purified by recrystallization, and then dissolved in water, and a stream of sulphuretted hydrogen passed through the solution. Zinc sulphide precipitates, and lactic acid is set free—



The solution of lactic acid is once more evaporated on the water-bath, the residue dissolved in a small quantity of water, and the solution shaken with ether, which dissolves the lactic acid. On pouring off the ethereal solution and evaporating, pure lactic acid remains as a colourless syrupy liquid, which cannot be distilled without decomposition. All the lactates are soluble in water. The alkaline lactates do not crystallize; calcium lactate,  $\text{Ca}(\text{C}_3\text{H}_5\text{O}_3)_2 \cdot 5\text{H}_2\text{O}$ , crystallizes tolerably well; but zinc lactate,  $\text{Zn}(\text{C}_3\text{H}_5\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$ , is the most characteristic salt, crystallizing in brilliant four-sided prisms.

**81. Ethereal Salts.**—The salts which the organic acids form with the alcohol radicals themselves remain to be spoken of.

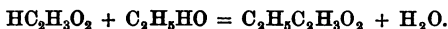
**82. Methyl Oxalate**,  $(\text{CH}_3)_2\text{C}_2\text{O}_4$ , is a crystalline compound, which is sometimes prepared as a means of obtaining pure methyl alcohol. It is easily obtained by the action of oxalic acid on methyl alcohol. Wood spirit is mixed with sulphuric acid and potassium binoxalate, and distilled in a retort. As soon as crystals of the oxalate begin to form in the neck of the retort the receiver is changed, and the distillation continued as long as fresh crystals form. The crystals are pressed between filtering paper, mixed with water and redistilled, when pure methyl alcohol (mixed with water) distils over, and oxalic acid remains behind in the retort.

**83. Methyl Acetate**,  $\text{CH}_3\text{C}_2\text{H}_3\text{O}_2$ , is a pleasant-smelling liquid, which boils at  $55^\circ$ . It is obtained by distilling methyl alcohol with a mixture of sodium acetate and sulphuric acid.

**84. Ethyl Formiate**,  $\text{C}_2\text{H}_5\text{CHO}_2$ , is isomeric with the foregoing, and boils at the same point,  $55^\circ$ . It is, how-

ever, easily distinguished, as it is decomposed by caustic potash into potassium formiate and alcohol, while methyl acetate yields potassium acetate and methyl alcohol. Ethyl formiate may be prepared by distilling sodium formiate with alcohol and sulphuric acid. It has an agreeable smell of peaches.

**85. Ethyl Acetate,  $C_2H_5C_2H_3O_2$ .**—This substance, commonly called *acetic ether*, is produced by the action of acetic acid on ethyl alcohol—



In order to prepare it, a mixture is made of one part of absolute alcohol with three parts of concentrated sulphuric acid. These are mixed carefully, and allowed to stand twenty-four hours. Sodium acetate is melted and allowed to cool, and two parts of this, in small pieces, are placed in a retort. The mixture of sulphuric acid and alcohol is poured on this, allowed to stand for twenty-four hours, and then distilled. The distillate is pure acetic ether, which may be dried over calcium chloride and redistilled. Ethyl acetate is a colourless liquid, possessing a pleasant refreshing smell, and boils at  $74^\circ$ .

**86. Ethyl Butyrate,  $C_2H_5C_4H_7O_2$ .**—Butyric ether is obtained by distilling together sodium butyrate, alcohol and sulphuric acid. It boils at  $119^\circ$ , and has a pleasant smell of pine-apples.

**87. Amyl Acetate,  $C_5H_{11}C_2H_3O_2$ ,** is obtained by distillation of amyl alcohol with sodium acetate and sulphuric acid. It boils at  $140^\circ$ , and has a pleasant smell of pears, whence its use for flavouring confectionary.

**88. Spermaceti** belongs to this class of ethereal salts or *compound ethers*, inasmuch as it is *cetyl palmitate*, having the formula  $(C_{16}H_{33})C_{16}H_{31}O_2$ .

**89. Anhydrides of the Organic Acids.**—The organic anhydrides bear the same relationship to the corresponding acids, as the inorganic anhydrides do to the inorganic acids. For example—

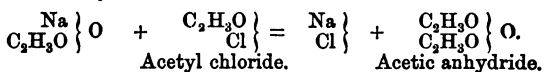
## MONATOMIC ACIDS.

Type.	Acid.	Anhydride.
$\begin{matrix} \text{H} \\ \text{H} \end{matrix} \left\{ \text{O} \right.$	$\begin{matrix} \text{NO}_2 \\ \text{H} \end{matrix} \left\{ \text{O} \right.$	$\begin{matrix} \text{NO}_2 \\ \text{NO}_2 \end{matrix} \left\{ \text{O} \right.$
	Nitric acid.	Nitric anhydride.
$\begin{matrix} \text{C}_2\text{H}_3\text{O} \\ \text{H} \end{matrix} \left\{ \text{O} \right.$	$\begin{matrix} \text{C}_2\text{H}_3\text{O} \\ \text{H} \end{matrix} \left\{ \text{O} \right.$	$\begin{matrix} \text{C}_2\text{H}_3\text{O} \\ \text{C}_2\text{H}_3\text{O} \end{matrix} \left\{ \text{O} \right.$
	Acetic acid.	Acetic anhydride.

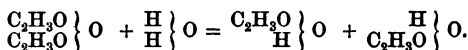
## DIATOMIC ACIDS.

$\begin{matrix} \text{H}_2 \\ \text{H}_2 \end{matrix} \left\{ \text{O}_2 \right.$	$\begin{matrix} \text{SO}_2 \\ \text{H}_2 \end{matrix} \left\{ \text{O}_2 \right.$	$\text{SO}_3$
	Sulphuric acid.	Sulphuric anhydride.
	$\begin{matrix} \text{C}_4\text{H}_4\text{O}_3 \\ \text{H}_2 \end{matrix} \left\{ \text{O}_2 \right.$	$\text{C}_4\text{H}_4\text{O}_3$
	Succinic acid.	Succinic anhydride.

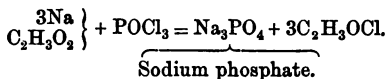
90. Acetic Anhydride,  $\begin{matrix} \text{C}_2\text{H}_3\text{O} \\ \text{C}_2\text{H}_3\text{O} \end{matrix} \left\{ \text{O} \right.$ , is obtained by the action of acetyl chloride on sodium acetate—



Acetic anhydride is a mobile liquid, boiling at 137°. It dissolves in water, forming acetic acid—



91. Acetic Oxychloride, or acetyl chloride,  $\text{C}_2\text{H}_3\text{OCl}$ , is obtained by the action of phosphorous oxychloride,  $\text{POCl}_3$  on sodium acetate—

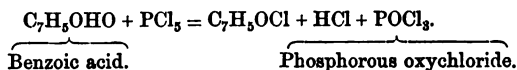


Acetyl chloride is a liquid which boils at 55°. It is decomposed by water into hydrochloric and acetic acids.

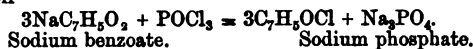
The oxychlorides and anhydrides of several other acids of this series have been obtained.

92. Benzoic Oxychloride,  $\text{C}_7\text{H}_5\text{OCl}$ , is obtained by dis-

tilling together benzoic acid and phosphoric chloride, when the following reaction takes place—

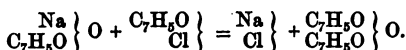


The mixture of benzoic oxychloride and phosphorous oxychloride may then be distilled with sodium benzoate, when the phosphorous oxychloride is decomposed, yielding again benzoic oxychloride, as shown in the following equation—



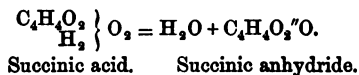
Benzoic oxychloride is a colourless liquid, possessing an irritating odour. It boils at 195°.

93. Benzoic Anhydride,  $\left. \begin{smallmatrix} \text{C}_7\text{H}_5\text{O} \\ \text{C}_7\text{H}_5\text{O} \end{smallmatrix} \right\} \text{O}$ , is obtained by acting upon sodium benzoate with benzoic oxychloride—



It is a white solid, which fuses at 42°, and boils at 310°.

94. Succinic Anhydride,  $\text{C}_4\text{H}_4\text{O}_3$ , may be taken as an example of the anhydride of a dibasic acid. It is obtained from succinic acid by simply abstracting water, which may be effected by distilling the acid with phosphoric anhydride—



95. Amines are substances derived from ammonia by the replacement of one or more atoms of hydrogen by alcohol

radicals, as phenylamine (aniline)— $\left. \begin{smallmatrix} \text{C}_6\text{H}_5 \\ \text{H} \\ \text{H} \end{smallmatrix} \right\} \text{N}$ , derived

from  $\left. \begin{smallmatrix} \text{H} \\ \text{H} \\ \text{H} \end{smallmatrix} \right\} \text{N}$ . Amines, derived from only one molecule of ammonia, are termed **monamines**; those from two mole-

cules, **diamines**; and from three molecules, **triamines**. Thus

phenylamine is a monamine; the substance  $\left. \begin{array}{c} \text{H} \\ \text{H} \\ \text{C}_2\text{H}_4 \\ \text{H} \\ \text{H} \end{array} \right\} \text{N},$  in

which the diatomic radical  $\text{C}_2\text{H}_4$ , unites the two molecules of ammonia, is a diamine, and so on. The monamines are further termed *primary*, *secondary*, or *tertiary*, according as one, two, or three atoms of hydrogen in the original ammonia, are replaced by alcohol radicals.

Thus  $\left. \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{H} \\ \text{H} \end{array} \right\} \text{N}$ , ethylamine, is a primary monamine;

$\left. \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{H} \end{array} \right\} \text{N}$ , or diethylamine, is a secondary monamine; and

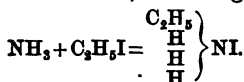
$\left. \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \right\} \text{N}$  is a tertiary monamine. It is not necessary

that the same radical should replace all the hydrogen atoms, so that we may have amines containing two or three different organic radicals. Thus we have the secondary

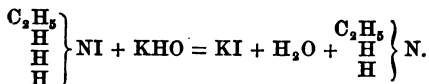
monamine, methyl ethylamine,  $\left. \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{CH}_3 \\ \text{H} \end{array} \right\} \text{N}$ , and the ter-

tiary monamine, methyl ethyl amylamine,  $\left. \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{CH}_3 \\ \text{C}_5\text{H}_{11} \end{array} \right\} \text{N}$ .

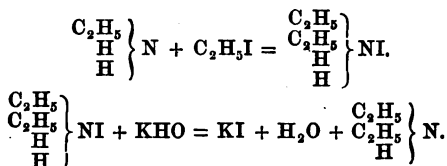
One general method by which the amines can be obtained consists in acting upon ammonia with the iodide of an alcohol radical, and then decomposing the substance obtained by distillation with caustic potash. Thus if ethyl iodide be heated with an alcoholic solution of ammonia, the two combine, according to the equation—



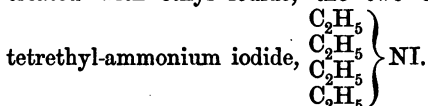
This substance—ethyl-ammonium iodide—is decomposed by distillation with caustic potash, yielding ethylamine—



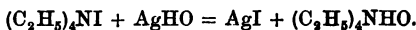
If this ethylamine be digested a second time with ethyl iodide, and the compound obtained be distilled with caustic potash, diethylamine is obtained—



By repeating these processes once more,  $\left. \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \right\} \text{N}$ , triethylamine is obtained. If now triethylamine be treated with ethyl iodide, the two combine, forming



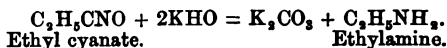
This substance is not decomposed by caustic potash; but, if a solution of the substance be treated with silver oxide, it is decomposed with the liberation of tetrethyl-ammonium hydrate—



The new substance is a solid, possessed of very strong basic properties. Like caustic potash, it absorbs carbonic anhydride and water from the air, and, like it, will saponify fatty substances, and precipitate metallic hydrates from solution of their salts. The substance is specially interesting, because it corresponds exactly to

the hypothetical ammonium hydrate, which has never been obtained.

Another general method of obtaining these amines is to decompose the cyanates of the alcohol radicals with caustic potash. If potassium-ethyl sulphate be distilled with potassium cyanate, a pungent volatile liquid is obtained, which contains  $C_2H_5CNO$ . If this be decomposed by caustic potash, potassium carbonate and ethylamine are obtained—



This is, in fact, the method by which these substances were first obtained.

96. Methylamine,  $\left. \begin{array}{c} CH_3 \\ H \\ H \end{array} \right\} N$ , is a gas at ordinary tem

peratures, but is condensed to a liquid in a freezing mixture. It strongly resembles ammonia, having the same pungent odour and intense alkaline reaction. It fumes with hydrochloric acid, but, unlike ammonia, burns easily. It is remarkable as being the most soluble gas known, forming a solution which precipitates metallic salts in the same way as the ordinary solution of ammonia does. Like ammonia, it dissolves copper hydrate, forming a deep blue solution. Methylamine hydrochlorate forms, with platinum chloride, a soluble compound (insoluble in alcohol), having the formula  $PtCl_4 \cdot 2CH_3NH_3Cl$ .

Dimethylamine,  $(CH_3)_2NH$ ; trimethylamine,  $(CH_3)_3N$ ; and tetramethyl-ammonium hydrate,  $(CH_3)_4NHO$ , can be obtained by the processes mentioned above.

97. Ethylamine,  $\left. \begin{array}{c} C_2H_5 \\ H \\ H \end{array} \right\} N$ , is a colourless liquid, boiling

at  $18^\circ$ . It combines with hydrochloric acid, forming  $N(C_2H_5)H_3Cl$ , which, with platinum chloride, yields the double salt  $PtCl_4 \cdot 2N(C_2H_5)H_3Cl$ .

Diethylamine,  $(C_2H_5)_2HN$ , boils at  $57^\circ$ . Triethyl-

amine,  $(C_2H_5)_3N$ , boils at  $91^\circ$ . Tetrethyl-ammonium hydrate is a solid substance.

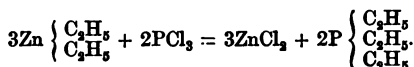
98. Propylamine,  $C_3H_7H_2N$ , is isomeric with trimethylamine,  $(CH_3)_3N$ . The two may be distinguished by treatment with an organic iodide such as ethyl iodide, and then with caustic potash. Propylamine will yield a

volatile base, viz., ethyl-propylamine,  $C_3H_7 \left\{ \begin{smallmatrix} C_2H_5 \\ H \end{smallmatrix} \right\} N$ ; whilst trimethylamine will form with the ethyl iodide a compound not decomposable by caustic potash.

Compounds analogous to those described are formed by phosphorus, arsenic, antimony, boron, and silicon with the alcohol radicals.

99. Triethyl Phosphine,  $C_2H_5 \left\{ \begin{smallmatrix} C_2H_5 \\ C_2H_5 \end{smallmatrix} \right\} P$ , is a colourless

liquid, possessing a powerful smell. It boils at  $127^\circ$ . It is obtained by the action of phosphorus trichloride on the substance zinc ethyl (to be afterwards described)—



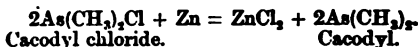
100. Arsenic Bases.—Arsenic is triatomic. If the three atoms of chlorine in arsenic chloride be successively replaced by methyl, we obtain the following compounds:—

$AsCl_3$ , .....	Arsenic trichloride.
$AsCH_3Cl_2$ , .....	Arsenmonomethyl chloride.
$As(CH_3)_2Cl$ , .....	Arsendimethyl chloride.
$As(CH_3)_3$ , .....	Trimethylarsine.

101. Trimethyl Arsine is a colourless liquid which boils at  $120^\circ$ .

102. Arsendimethyl.— $As(CH_3)_2$  is a monatomic radical, and has in the free state the formula  $\left\{ \begin{smallmatrix} As(CH_3)_2 \\ As(CH_3)_2 \end{smallmatrix} \right\}$ . It has received the name cacodyl, in allusion to its disagreeable odour. It is a colourless liquid boiling at  $170^\circ$ .

It forms an oxide  $\text{As}_2(\text{CH}_3)_4\text{O}$ , obtained by heating arsenous anhydride with potassium acetate. The action of hydrochloric acid on this yields cacodyl chloride, which, on treatment with zinc, yields cacodyl itself.



Cacodyl and its compounds are fearfully poisonous. Cacodyl itself exhibits the remarkable property of spontaneous inflammability, taking fire on exposure to the air. It must therefore be prepared and preserved in vessels from which the air is excluded.

103. **Cacodyl Cyanide** is a beautifully crystalline substance, which is, however, one of the most deadly poisons known.

104. Triethyl Stibine,  $\left. \begin{matrix} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{matrix} \right\} \text{Sb}$ , is a liquid, boiling at

$158^\circ$ , which takes fire spontaneously in the air. Boron forms with ethyl the compound borethyl,  $(\text{C}_2\text{H}_5)_3\text{B}$ , and silicon forms silicon ethyl, which contains  $(\text{C}_2\text{H}_5)_4\text{Si}$ .

Ethyl forms with zinc the compound zinc ethyl  $\text{Zn}(\text{C}_2\text{H}_5)_2$ , a liquid which boils at  $118^\circ$ , and which takes fire when it is exposed to the air. Mercury forms  $\text{Hg}(\text{C}_2\text{H}_5)_2$ , an excessively dangerous poison; lead forms  $\text{Pb}(\text{C}_2\text{H}_5)_2$ ; and sodium forms  $\text{NaC}_2\text{H}_5$ .

105. **Amides and Nitriles.**—If the hydrogen in ammonia be replaced, not by an alcohol radical, but by the oxidized radical of an acid, we obtain an amide instead of an amine. Thus from acetic acid,  $\left. \begin{matrix} \text{C}_2\text{H}_3\text{O} \\ \text{H} \end{matrix} \right\} \text{O}$ , we obtain

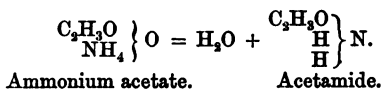
acetamide,  $\left. \begin{matrix} \text{C}_2\text{H}_3\text{O} \\ \text{H} \\ \text{H} \end{matrix} \right\} \text{N}$ ; or an amide may be said to be

derived from an acid by replacing the hydroxyl of the group  $\text{COH}$ , which every acid contains, by the monatomic group

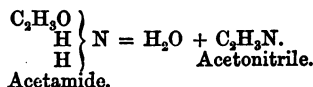
$\text{NH}_2$ ; so from acetic acid,  $\left\{ \begin{matrix} \text{CH}_3 \\ \text{COH} \end{matrix} \right.$ , we obtain acetamide,

$\left\{ \begin{array}{l} \text{CH}_3 \\ \text{CO}(\text{NH}_2) \end{array} \right\}$ . The amides, like the amines, are divided, first, into **monamides**, **diamides**, and **triamides**, according as they are derived from one, two, or three molecules of ammonia; and then into primary, secondary, and tertiary. Thus we have the primary monamide,  $\text{C}_2\text{H}_5\text{ONH}_2$ , or acetamide; the secondary monamide,  $(\text{C}_2\text{H}_5\text{O})_2\text{NH}$ , or diacetamide; and the tertiary monamide,  $(\text{C}_2\text{H}_5\text{O})_3\text{N}$ , or triacetamide.

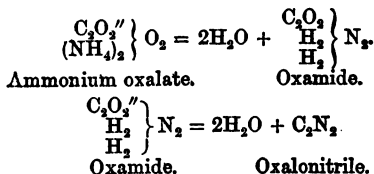
The amides can be obtained by abstracting the elements of water from the ammonium salts of the organic acid. Thus, if water be withdrawn from ammonium acetate we obtain acetamide—



If we proceed further, and by distilling the acetamide with phosphoric anhydride, remove another atom of water, we obtain the substance called **acetonitrile**—

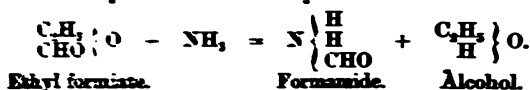


Acetonitrile may be regarded then as a compound of nitrogen with the triatomic radical ethenyl,  $\text{C}_2\text{H}_3'''$ . If we take oxalic acid, we can obtain in the same way **oxamide** and **oxalonitrile**. Oxalic acid being dibasic, oxamide is one of the diamides—

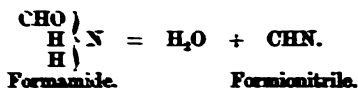


Oxalonitrile is the substance already described as **cyanogen**.

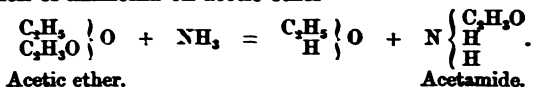
**106. Formamide.**  $\begin{matrix} \text{CHO} \\ | \\ \text{H} \\ | \\ \text{H} \end{matrix} \text{N}$  is a liquid boiling at  $194^\circ$ . It is obtained by the action of ethyl formiate on ammonia—



By heating with phosphoric anhydride, it is converted into *formionitrile*, which is identical with hydrocyanic acid—

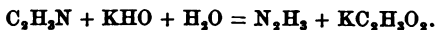


**107. Acetamide,**  $\begin{matrix} \text{C}_2\text{H}_5\text{O} \\ | \\ \text{H} \\ | \\ \text{H} \end{matrix} \text{N}$ , is best obtained by the action of ammonia on acetic ether—



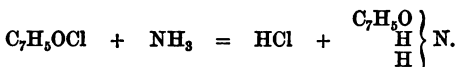
Acetamide is a white solid, melting at  $78^\circ \text{C}$ ., and boiling at  $221^\circ$ . When distilled with phosphoric anhydride, it loses water, and is converted into acetonitrile.

**108. Acetonitrile,**  $\text{C}_2\text{H}_3\text{N}$ , is a liquid, boiling at  $77^\circ$ . It is isomeric, but not identical with the true methyl cyanide, which is a liquid boiling at  $58^\circ$ . Acetonitrile is decomposed by caustic potash, yielding ammonia and acetic acid—



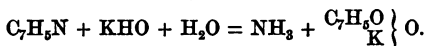
In the same way, *propionitrile* has the same formula as ethyl cyanide, *butyronitrile* as propyl cyanide, and so on.

**109. Benzamide,**  $\begin{matrix} \text{C}_7\text{H}_5\text{O} \\ | \\ \text{H} \\ | \\ \text{H} \end{matrix} \text{N}$ , is obtained by the action of ammonia on benzoic oxychloride—

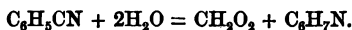


It is a white solid, which melts at  $115^\circ \text{C}$ .

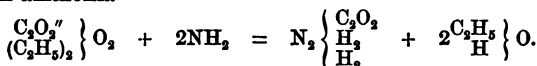
**110. Benzonitrile**,  $\text{C}_7\text{H}_5\text{N}$ , can be obtained by distilling benzamide with phosphoric anhydride. It is a liquid which boils at  $191^\circ$ . It is decomposed by caustic potash, yielding ammonia and potassium benzoate—



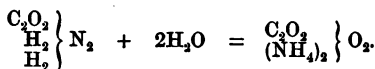
Phenyl cyanide is isomeric with this, but different in properties. It is not decomposed by alkalies, but is by acids, yielding formic acid and aniline—



**111. Oxamide**,  $\text{C}_2\text{O}_2 \left\{ \begin{smallmatrix} \text{H}_2 \\ \text{H}_2 \end{smallmatrix} \right\} \text{N}_2$ , may be obtained either by distilling ammonium oxalate, or by acting on oxalic ether with ammonia—

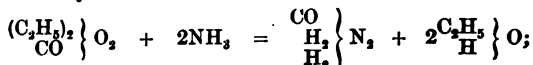


Oxamide is a solid substance, which loses water on heating with phosphoric anhydride, passing into oxalonitrile; and which takes up water on heating with it under pressure, passing into ammonium oxalate—

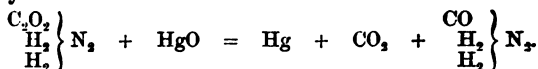


**112. Carbamide or Urea**,  $\text{CO}'' \left\{ \begin{smallmatrix} \text{H}_2 \\ \text{H}_2 \end{smallmatrix} \right\} \text{N}_2$ , is the diamide derived from carbonic acid, the formula of which may be written  $\text{CO}'' \left\{ \begin{smallmatrix} \text{H}_2 \\ \text{H}_2 \end{smallmatrix} \right\} \text{O}_2$ . Urea is found in considerable quantity in the urine of mammalia, and may be obtained artificially in several ways. Its mode of formation from ammonium

cyanate has been already mentioned. It may also be obtained by the action of ammonia on carbonic ether—



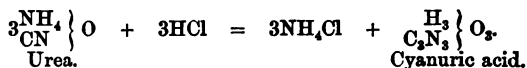
or by the action of mercuric oxide on oxanide—



Urea crystallizes in long needles, which are soluble in water and alcohol.

When heated with water in closed tubes, it produces ammonia and carbonic acid.

Urea is decomposed when heated in dry hydrochloric acid with formation of cyanuric acid—



**113. Vegeto-Alkaloids.**—Certain plants contain nitrogenous substances, possessing basic properties, which are probably compound ammonias, though they have not been artificially prepared.

Some few contain only carbon, hydrogen, and nitrogen, but most contain also oxygen.

They nearly all combine with hydrochloric acid and platinum chloride to form double salts, which are commonly insoluble in water, or only difficultly soluble.

**114. Conine**,  $\text{C}_8\text{H}_{15}\text{N}$ , is contained in hemlock. It is a colourless liquid, boiling at  $163^\circ$ , and which is poisonous.

**115. Nicotine**,  $\text{C}_{10}\text{H}_{14}\text{N}_2$ , is obtained from tobacco. It is a very poisonous oil, which boils at about  $250^\circ$ , being partly decomposed.

**116. Piperine**,  $\text{C}_{17}\text{H}_{19}\text{NO}_3$ , is contained in pepper. By distillation with caustic potash it yields piperidine,  $\text{C}_5\text{H}_{11}\text{N}$ , a liquid boiling at  $106^\circ$ , and smelling of ammonia and pepper.

**117. Opium Alkaloids.**—Opium is the dried juice of

certain kinds of poppy. It contains an acid called *meconic acid*, and seven alkaloids—

Morphine, .....	$C_{17}H_{19}NO_3$
Codeine, .....	$C_{18}H_{21}NO_3$
Thebaine, .....	$C_{19}H_{21}NO_3$
Papaverine, .....	$C_{20}H_{21}NO_4$
Narcotine, .....	$C_{25}H_{25}NO_7$
Cryptopine, .....	$C_{28}H_{25}NO_5$
Narceine, .....	$C_{29}H_{29}NO_9$

Of these morphine is the most important, though most of the others have also a strong action on the animal system.

**118. Morphine.**—The best opium contains about 12 per cent. of morphine. In order to extract morphine from opium, an infusion of the drug in water is made, and filtered through linen. The clear solution is concentrated, and mixed with chalk to render it neutral. Calcium-chloride solution is then added, when a precipitate of calcium meconate is obtained, and morphine hydrochlorate remains in solution. The liquid is filtered and evaporated, when, on cooling, crystals of morphine hydrochlorate separate out.

Morphine requires 1000 times its own weight of cold water to dissolve it, but it dissolves easily in alcohol. It is insoluble in ether and in chloroform. Morphia may be detected by the production of a blue colour when neutral solution of ferric chloride is added. Nitric acid colours morphine yellow; a mixture of nitric and sulphuric acids colours it green.

Morphine is a valuable medicine in small doses. It acts as a sedative; but in large quantities is a narcotic poison.

It forms salts, which crystallize well.

The hydrochlorate contains  $C_{17}H_{19}NO_3HCl$ ; the sulphate,  $(C_{17}H_{19}NO_3)_2H_2SO_4$ .

**119. Strychnine and Brucine** are contained in the seeds of *nux vomica*, and in *St. Ignatius's bean*. They both act as violent poisons, causing death with tetanic convulsions.

**120. Strychnine** contains  $C_{21}H_{22}N_2O_4$ . The St. Ignatius bean contains 1 or 2 per cent. of strychnine. Strychnine crystallizes easily. It is insoluble in alcohol, and water takes up only  $\frac{1}{70000}$  of its weight, forming, however, an intensely bitter solution. Strychnine forms salts, which crystallize easily. Strychnine can be detected, even in very small quantity, by the violet colour produced by the action on it of sulphuric acid and potassium bichromate.

**121. Brucine** contains  $C_{23}H_{26}N_2O_4$ ; it is more soluble in water and alcohol than strychnine. It is a usual impurity in commercial strychnine. It may be detected by the bright red colour it produces when moistened with nitric acid. (Brucine forms also a delicate test for nitric acid).

Brucine is somewhat less poisonous than strychnine.

**122. Quinine**,  $C_{20}H_{24}N_2O_2$ , is contained, together with cinchonine, in Peruvian bark, the bark of several species of cinchona. The cinchonas are natives of Peru, but are now grown in India and Java. To extract quinine the bark is boiled with dilute sulphuric acid, which dissolves out the quinine and cinchonine as sulphates. To the filtered solution, sodium carbonate is added, and the precipitate containing the bases is treated with hot alcohol. On cooling, the bulk of the cinchonine crystallizes out, and the quinine remains in solution. To complete the separation the alkaloids are converted into sulphates and crystallized. The quinine sulphate, which is least soluble, crystallizes out first, and the quinine itself may be precipitated by adding ammonia to the solution of the sulphate; or quinine may be separated from cinchonine by means of ether, in which quinine dissolves, whilst cinchonine is insoluble.

Quinine requires 350 times its own weight of water to dissolve it. It dissolves much more easily in alcohol. Quinine is employed in medicine principally as quinine sulphate  $(C_{20}H_{20}N_2O_2)_2H_2SO_4$ , a salt which is only sparingly soluble in water, but dissolves easily in dilute

sulphuric acid. Solutions of quinine exhibit the phenomenon of fluorescence very distinctly, giving out a blue light when illuminated by sunlight. Quinine and its salts possess an intensely bitter taste. A solution of quinine has a peculiar action on polarized light transmitted through it, rotating the plane of polarization to the left. Quinine may be detected by the green colour produced on adding to a solution of the sulphate, first, chlorine water, and then ammonia in excess.

**123. Cinchonine**,  $C_{20}H_{24}N_2O$ , does not possess the same valuable medicinal properties as quinine. It has a bitter taste like quinine, and is a strong base, forming salts which are generally less soluble than the corresponding salts of quinine. Cinchonine produces an effect on polarized light exactly opposite to that produced by quinine, rotating the plane of polarization to the right. Cinchonidine and cinchonidine are alkaloids isomeric with cinchonine. In like manner there exist two alkaloids isomeric with quinine, viz., quinidine and quinicine. These differ remarkably in their action on polarized light, as shown in the following table:—

Left-handed.	Right-handed.
Quinine, .....strongly.	Cinchonine, .....strongly.
Cinchonidine .....strongly.	Quinidine, .....strongly.
Quinicine, .....feebly.	Cinchonidine, .....feebly.

**124. Theine or Caffeine**,  $C_8H_{10}N_4O_2$ , is contained in tea and coffee. Cocoa contains theobromine,  $C_7H_8N_4O_2$ , which differs from caffeine by containing  $CH_2$  less.

**125. Atropine**,  $C_{17}H_{23}NO_3$ , is contained in belladonna. Its salts are highly poisonous.

**126. Sugars and Allied Substances.**—These all appear to contain six atoms of carbon, or a multiple of that number, united with hydrogen and oxygen in the proportions in which they combine to form water. They may be divided into three groups, as shown in the following tables, where the action of each variety on polarized light is also stated:—

GROUP I.—FORMULA,  $C_{12}H_{22}O_{11}$ .

Cane sugar or Sucrose,.....	Right-handed.
Milk sugar or Lactose,.....	Right-handed.
Mycose or Trehalose,.....	Right-handed.
Melezitose,.....	Right-handed.
Mycose,.....	Right-handed.

GROUP II.—FORMULA,  $C_6H_{12}O_6$ .

Grape sugar or Dextrose,.....	Right-handed.
Fruit sugar or Levulose,.....	Left-handed.
Galactose,.....	Left-handed.
Sorbin,.....	Left-handed.
Eucalin,.....	Left-handed.

GROUP III.—FORMULA,  $C_6H_{10}O_5$ .

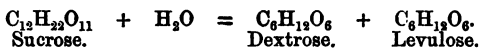
Starch,.....	Right-handed.
Glycogene,.....	Right-handed.
Dextrine,.....	Right-handed.
Inuline,.....	Left-handed.
Gums.	
Cellulose.	

127. Cane Sugar,  $C_{12}H_{22}O_{11}$ , is a common product of plant life. It is obtained principally from the sugar cane, the beet-root, and the sugar maple. The expressed juice of the cane is mixed with milk of lime to neutralize free acid, then heated to boiling, and evaporated as rapidly as possible. On cooling, sugar crystallizes out. A second crop of crystals is obtained by further evaporating the mother liquor; the dark-coloured uncrystallizable sugar which is left behind is molasses or treacle.

The brown sugar imported into England is subjected to the refining process in order to convert it into white loaf sugar. For this purpose it is dissolved in water, mixed with a little lime, and boiled. The dark-coloured liquid is then allowed to run through filters filled with animal charcoal, which has the power of absorbing the colouring matter, and a colourless syrup runs from the filters. This is then evaporated in vacuum pans—closed pans from which the air and steam is being continually removed by an air-pump. The syrup is thus evaporated at a low temperature, and the prejudicial formation of *sugar which will not crystallize* is avoided.

Sugar has a specific gravity of 1.606. It is soluble in one-third of its weight of cold water, and is freely soluble in hot water; it is nearly insoluble in alcohol.

If a solution of sugar be long boiled, more especially if the solution be acid, a considerable portion loses the property of crystallizing, in consequence of the formation of the uncrystallizable levulose. Dextrose is formed at the same time.



The same change is brought about by yeast. Cane sugar is not itself capable of being fermented, but both dextrose and levulose are.

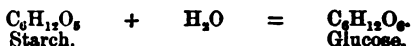
Sugar is capable of combining with some inorganic bases and salts to form definite compounds. Thus lime is much more soluble in solutions of sugar than in water, in consequence of the formation of the compound  $\text{C}_{12}\text{H}_{22}\text{O}_{11}\text{CaO}$ . A solution of cane sugar has a definite amount of action on polarized light, rotating the plane of polarization to the right, through an angle depending on the strength of the solution, and this property is made use of in determining the strength of sugar solutions during the refining process, &c.

Gold is reduced from its salts by boiling their solutions with sugar. Copper in alkaline solutions is scarcely reduced, a reaction which serves to distinguish cane sugar from grape sugar.

**128. Milk Sugar** occurs in the milk of mammalia, and is obtained by evaporating the sweet milk. It is not so soluble in water, nor so sweet as cane sugar. Its specific gravity is 1.54. It turns the plane of polarization to the right, but not so strongly as cane sugar. It does not ferment like cane-sugar; but in presence of cheese, the peculiar fermentation termed the lactic takes place, lactic acid being formed. Lactose precipitates red cuprous oxide from alkaline solutions of cupric salts, even in the cold. By boiling with dilute acids, lactose is converted into the left-handed galactose.

**129. Grape Sugar, dextrose,  $C_6H_{12}O_6$ ,** occurs in most ripe fruits, and is also a constituent of honey. It may be obtained from honey by treating it with cold alcohol, which dissolves out the more soluble levulose also contained in honey; and by recrystallization from boiling alcohol the dextrose may be obtained pure.

Starch may be converted into dextrose by boiling it with a dilute acid; and dextrose is manufactured in this way, on a somewhat large scale, by allowing a thin mixture of starch with water to flow gradually into a vat containing boiling dilute sulphuric acid. After boiling for about an hour, the liquid is neutralized with chalk, the precipitate allowed to subside, and the clear liquid concentrated and allowed to crystallize. The change by which starch is converted into sugar consists simply in the assimilation of water—



Grape sugar is much less sweet than cane sugar. It is less soluble in water, but more soluble in alcohol.

Grape sugar precipitates metallic silver from solutions of silver salts in the form of a brilliant metallic mirror. It also precipitates red cuprous oxide from an alkaline solution of a copper salt, and can thus be distinguished from cane sugar. By using a standard solution of copper we can determine the quantity of grape sugar present in a solution. Dextrose has a strong action on polarized light, turning the plane of polarization to the right.

**130. Levulose, Fruit Sugar or Inverted Sugar,  $C_6H_{12}O_6$ ,** occurs in honey and many fruits, together with dextrose; and is formed, together with dextrose, by the action of acids on cane sugar. To prepare it, the cane sugar which has been treated with acid is mixed with lime, and filtered through linen. Ordinary grape sugar passes through, while the levulose remains behind in the form of an insoluble compound with lime which may be decomposed with oxalic acid in order to obtain the sugar. Levulose

rotates the plane of polarization to the left much more strongly when cold than when hot.

It forms a colourless uncrystallizable syrup, more soluble in water than grape sugar, and sweeter.

Sugar, in common with many other organic substances, undergoes **fermentation** under certain conditions. The fermentation is brought about by the presence of some **ferment** which sets up the decomposition—the part played by *yeast* in the ordinary alcoholic fermentation by which sugar is converted into alcohol. The products of fermentation vary with the nature of the substance subjected to the process, and with the nature of the ferment, so that we have several distinct kinds of fermentation. In the *alcoholic* fermentation, alcohol and carbon dioxide are the principal products; the *acetous* fermentation yields acetic acid; the *lactic* fermentation and the *butyric*, lactic and butyric acids respectively. In many cases fermentation (and putrefaction, which is a kind of fermentation) seems to take place when no ferment has been added. It has, however, been shown that in these cases the fermentible substances obtain the necessary ferment from the air, and that minute living organisms, the *sporules*, which give rise to the fermentation, are always floating about in the air. If the germs already present in any fermentible liquid be killed by exposing the liquid to a sufficiently high temperature, and if then the air be excluded, no fermentation or putrefaction takes place; or if only air be admitted which has been passed through thin red hot tubes, or which has been filtered through tightly packed cotton wool, then also no fermentation takes place.

The various varieties of sugar possessing the formula,  $C_6H_{12}O_6$  are all capable of undergoing the alcoholic fermentation. Cane sugar also can be fermented in the presence of yeast, but it first of all takes up water and becomes grape sugar.

The fermentation takes place only at a particular temperature, best at  $25^\circ$  or  $30^\circ$ .

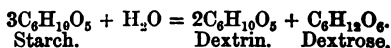
The following equation represents the change—



Small quantities of glycerin and of succinic acid are produced at the same time.

**131. Starch**,  $C_6H_{10}O_5$ , is contained in the roots, stems, and seeds of many plants. It is obtained from wheat, and other kinds of grain, and from potatoes, and other roots. Sago, Indian corn, &c., are also varieties of starch. Starch is a white powder, which under the microscope is seen to consist of very fine granules, each possessing a distinct structure. Starch is insoluble in cold water, but if boiled with water the granules swell and burst, and starch paste is obtained. By boiling for a length of time starch is partly rendered soluble in water. Free iodine colours starch blue, a reaction which is not obtained with gum or the other substances of the same composition as starch.

The starch contained in seeds undergoes a sort of fermentation during the germination of the seeds, by which it is converted into dextrin and grape sugar, as shown in the following equation :—



This is the change which takes place in the malting of barley. The barley is allowed to germinate up to a certain point, and the growth is then stopped by applying heat. If the malt be infused in warm water, a saccharine liquid is obtained, capable of being fermented. Dilute sulphuric acid acts upon starch so as to bring about a similar change. If starch be heated to  $160^\circ$ , it is converted into dextrin.

**132. Dextrin**,  $C_6H_{10}O_5$ , is obtained by heating starch to a temperature of  $150^\circ$  to  $200^\circ$ . It is largely prepared in this way, and is employed as a substitute for gum, under the name British gum.

It is obtained, together with dextrose, by the action of an infusion of malt on starch, the change being brought

about by the influence of the peculiar ferment contained in malt, which has been called **diastase**. It is for this reason that distillers mix unmalted barley with their malt in preparing the **wort**, which is to be fermented. An infusion is obtained which is as sweet as if the same weight of malt were employed, the starch in the unmalted barley being converted by the diastase of the malt into dextrin and dextrose. Dextrin is not turned blue by iodine as starch is.

**133. Gum Arabic** is an exudation from various species of acacia.

**134. Cellulose** is the substance out of which the woody fibre of plants is constructed. It is contained in a nearly pure state in cotton wool. It has the same composition as gum and starch. It is insoluble in water, alcohol, and ether; but dissolves in an ammoniacal solution of copper oxide.

Cellulose is acted upon by nitric acid in a peculiar manner. If cotton wool or paper be soaked in strong nitric acid, and then washed in plenty of water, a substance is obtained which has outwardly the same appearance as the original material, but which is very inflammable, being the substance known as gun-cotton, or gun-paper. It is cellulose in which three atoms of hydrogen have become displaced by three atoms of  $\text{NO}_2$ , the radical of nitric acid, so that gun-cotton has the formula  $\text{C}_6\text{H}_7(\text{NO}_2)_3\text{O}_5$ . Gun-cotton dissolves in ether, forming the substance known as *collodion*, which is employed in photography.

**135. Analytical Detection of the Organic Acids.**—The following acids only are considered:—*Hydrocyanic, oxalic, tartaric, citric, and acetic.*

**136. Hydrocyanic Acid.**—The alkaline cyanides are soluble in water, but are decomposed by acids, even by acetic, with liberation of gaseous hydrocyanic acid. Mercuric cyanide,  $\text{HgCy}_2$ , is soluble in water. Most of the other cyanides are insoluble.

If to a solution of hydrocyanic acid, or an alkaline

cyanide, caustic potash be added, and then a mixed solution of ferrous and ferric salt, a greenish blue precipitate separates; and, on adding hydrochloric acid in excess, a precipitate of Prussian blue remains.

If a solution containing hydrocyanic acid be mixed with a few drops of yellow ammonium sulphate, and the mixture be evaporated at  $100^{\circ}$ , till the excess of ammonium sulphate has been expelled; then, on adding a drop of ferric chloride, a deep red colouration of ferric sulphocyanide is obtained.

Silver cyanide is insoluble in diluted nitric acid. On ignition, it yields metallic silver.

In cases where the liquid suspected to contain hydrocyanic acid is a complicated organic mixture, it may be distilled with a dilute acid, and the distillate may be subjected to the above tests.

**137. Oxalic Acid.**—Oxalic acid and the oxalates of the alkaline metals are soluble in water. Most of the other oxalates are insoluble in water, but soluble in dilute acids. The oxalates are decomposed on ignition, the oxalates of silver, copper, &c., giving the metal, while the oxalates of barium, calcium, &c., yield the carbonates of these metals, which on treatment with dilute hydrochloric acid effervesce, giving off carbon dioxide.

Oxalic acid or any oxalate is decomposed by boiling with concentrated sulphuric acid, giving off carbon dioxide and carbon monoxide; the gas burns at the mouth of the test tube with a blue flame. An oxalate is not decomposed by dilute sulphuric acid; but if manganese dioxide be added, an evolution of carbon dioxide takes place—



Calcium chloride produces, even in dilute solutions of oxalates, a white precipitate of calcium oxalate, insoluble in acetic acid, soluble in hydrochloric.

**138. Tartaric Acid.**—Tartaric acid and tartrates blacken on heating, evolving a characteristic smell resembling that of burnt sugar. Hot sulphuric acid also decomposes the

tartrates, with separation of carbon. Calcium chloride gives a white precipitate in neutral solutions of the tartrates, which is soluble in acids. The precipitate also dissolves in cold caustic potash, and is reprecipitated on boiling the solution.

**139. Citric Acid.**—Citric acid and citrates blacken on heating, giving a pungent smell different from that obtained on heating tartaric acid. When boiled with sulphuric acid, blackening takes place only after long boiling.

Calcium chloride produces in solutions of citrates (but not with free citric acid) a precipitate of calcium citrate, more insoluble in hot water than in cold, insoluble in caustic potash, but soluble in solution of ammonium chloride, and reprecipitated on boiling.

**140. Acetic Acid.**—Most of the acetates are soluble in water. When an acetate is heated with sulphuric acid, acetic acid is given off, which may be recognized by its smell, but no blackening takes place.

When an acetate is heated with sulphuric acid and alcohol, acetic ether is given off which possesses a characteristic smell.

#### **141. Detection of the Acids in a Mixture of their Sodium Salts.**

In testing for the organic acids it is necessary that the acids should be combined only with the alkaline metals. To get rid of the other metals sulphuretted hydrogen must sometimes be passed through the solution ; but generally it is sufficient to boil the solution with a slight excess of sodium carbonate. The heavy metals are then precipitated as carbonates, and the acids remain in solution as sodium salts.

The solution should be neutral. To obtain this a slight excess of nitric acid may be added, and the solution may then be boiled to expel carbonic anhydride. Ammonia is then added in very slight excess, and the solution is once more boiled till neutral to test paper. If the original solution contained ammonium salts, it must be boiled with

the ammonia: and it must then be evaporated to dryness. The residue may be evaporated to dryness. In all experiments with the substance, it blackens on heating in a test tube. In citric acid is present. In strong sulphuric acid is present. In tartaric acid is present. In citric acid is present.

These solutions may be mixed in the volumetric flask, and the solution and lime water added to the volumetric flask. The filtrate and tartrate will be precipitated. The filtrate be boiled, calcium tartrate (see B), and the filtrate be filtered. The filtrate be filtered, if hydrocyanic acids, if the filtrate is filtered by nitric acid, the filtrate is filtered. If hydrocyanic acid is present, the filtrate will be formed. The filtrate will be formed in the filtrate.

It is a white solid, is treated with cold caustic soda solution, is soluble in acids and is reprecipitated from the acid solution as a white or pinkish calcium salt. The solid is dissolved with dilute acetic acid and the solution is used for confirmatory tests may

On addition of 10 ml. of concentrated hydrochloric acid to red-brown residue, the residue will be calcium carbonate, which will give off carbon dioxide on treatment with dilute hydrochloric acid.

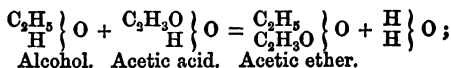
10. A portion of the precipitate may be mixed with dilute sulphuric acid. Then, on adding manganese dioxide, an evolution of carbon dioxide will take place. The presence of tartaric acid may be confirmed by heating a portion of the precipitate A to redness, and observing the blackening and characteristic smell obtained if tartaric acid is present.

The precipitate B may be dried and heated to redness,

when the odour characteristic of citric acid will be observed.

The precipitate C may be decomposed by a slight excess of ammonium sulphide, the filtrate evaporated to dryness, and the residue dissolved in a drop of water; then on adding ferric chloride, the characteristic red colouration will be obtained; or the precipitate may be decomposed by hydrochloric acid, and the filtrate subjected to the Prussian blue test. Lastly, acetic acid may be detected in the final precipitate by the odour of acetic ether obtained by distilling it with sulphuric acid and alcohol.

**142. Empirical and Rational Formulæ.**—The *empirical formula* of a substance is the simplest formula which expresses its composition; the *rational formula* seeks to express also the mode of formation of the substance, the decompositions which it undergoes, the specific gravity of its vapour, and its other physical properties. Thus, by distilling together acetic acid and alcohol we obtain a substance called acetic ether, whose *empirical formula* is  $C_2H_4O$ , but its mode of formation shows that this is not its true formula. The action by which it is obtained is represented by the equation—



and the rational formula is therefore  $\begin{array}{c} C_2H_5 \\ C_2H_3O \end{array} \left\{ O, O \right.$   
 $C_4H_8O_2$ .



# PAPERS SET IN ORGANIC CHEMISTRY

AT THE

## EXAMINATIONS OF THE SCIENCE AND ART DEPARTMENT, WITH ANSWERS.

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1868.

### INSTRUCTIONS.

You are only permitted to attempt *eight* questions.  
You may select these from any part of the paper.

Whenever possible, you are to express the reactions in equations.

You are to give such numerical details as will show the mode of calculation.

Atomic weights to be used:—

H = 1  
O = 16  
C = 12  
N = 14

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1. The formula of urea is  $\text{CN}_2\text{H}_4\text{O}$ , what is its percentage composition?

C	12	60	:	100	::	12	:	percentage of carbon.
N <sub>2</sub>	28	60	:	100	::	28	:	percentage of nitrogen.
H <sub>4</sub>	4	60	:	100	::	4	:	percentage of hydrogen.
O	16	60	:	100	::	16	:	percentage of oxygen.
	<hr/>	60						

Whence we have—

Carbon, .....	20.00
Nitrogen, .....	46.67
Hydrogen, .....	6.66
Oxygen, .....	26.67
	<hr/> 100.00

2. Give the formula and percentage composition of marsh gas.

Formula of marsh gas,  $\text{CH}_4$ .

Percentage composition found as above—

Carbon, .....	75.00
Hydrogen, .....	25.00
	<hr/> 100.00

3. When a powerful voltaic current passes between two pieces of gas carbon in an atmosphere of hydrogen, what chemical transformation is effected?

The carbon and hydrogen combine to form the hydrocarbon *acetylene*,  $\text{C}_2\text{H}_2$ .

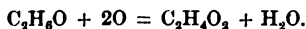
4. How can you obtain acetic acid from alcohol?

See p. 70. Alcohol can be converted into acetic acid by several different processes of *oxidation* :—

a. The alcohol may be oxidized by allowing it to drop slowly upon platinum black, so that the alcohol and the oxygen of the air come in contact in presence of the finely divided platinum.

b. The alcohol may be oxidized by boiling it with chromic acid, or with a mixture of sulphuric acid and potassium anhydro-chromate.

c. The alcohol may be oxidized by exposing it to the acetous fermentation (as described in p. 71). In all these cases water is separated according to the equation—



5. What is the composition of the organic acid con-

tained in ants? Can you obtain this acid from any other source?

Formic acid,  $\text{CH}_2\text{O}_2$ . It may be also obtained by the oxidation of methyl alcohol, and by the decomposition of oxalic acid, as described at p. 50.

6. Whence is methylic alcohol obtained, and how does it differ in composition from ethylic alcohol?

See p. 52.

7. How can you detect hydrocyanic acid?

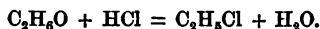
See p. 49.

8. How is ether made, and what is its formula?

See p. 59.

9. What happens when hydrochloric acid gas is passed into absolute alcohol?

Ethyl chloride or hydrochloric ether is formed, according to the equation—



See p. 63.

10. What is the formula of chloroform, and how would you obtain this body from ethylic alcohol?

$\text{CHCl}_3$ . It is prepared by distilling alcohol with bleaching powder. See p. 44.

11. How would you prepare olefiant gas?

See p. 32.

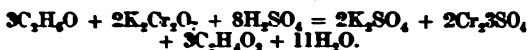
12. What is the composition of the liquid formed by the admixture of equal volumes of chlorine and olefiant gas?

Dutch liquid or ethylene dichloride,  $\text{C}_2\text{H}_4\text{Cl}_2$ .

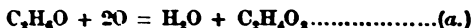
## 1869.

1. When alcohol is boiled with dipotassic dichromate (bichromate of potash) what acid product is obtained?

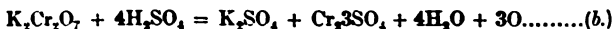
Acetic acid, according to the equation—



It may be useful to indicate how such an equation is got at. We know that the oxidation of alcohol by which it is converted into acetic acid is—



In this case the oxygen is obtained from  $K_2Cr_2O_7$  and  $SO_4H_2$ , which, when boiled together, give  $K_2SO_4$ ,  $Cr_2(SO_4)_3$ , and  $H_2O$ . It is clear, then, that  $K_2Cr_2O_7$  will require  $4H_2SO_4$  for decomposition, and will give off  $3O$ , according to the equation—



If now we multiply equation (a) all through by 3, and equation (b) by 2, we shall have the same quantity of oxygen in each case. Hence, we have simply to add together the two equations, and strike out the  $6O$  from each side, when we obtain the equation already given.

2. How would you estimate by analysis the percentage of carbon and hydrogen in an organic body?

See p. 11.

3. What is the empirical formula of a substance possessing the following percentage composition:—

Carbon, .....	40.00
Hydrogen, .....	6.66
Oxygen, .....	53.34
	<hr/>
	100.00

To ascertain this, we must divide each number by the atomic weight of the element—

$$\begin{array}{l} \text{C } 40.00 \div 12 = 3.33 \\ \text{H } 6.66 \div 1 = 6.66 \\ \text{O } 53.34 \div 16 = 3.33 \end{array}$$

Since the numbers obtained for C and H are the same, and that for H just double, the simplest formula of the substance is  $\text{CH}_2\text{O}$ , which is the answer required. The substance may be acetic acid,  $\text{C}_2\text{H}_4\text{O}_2$ , or lactic acid  $\text{C}_3\text{H}_5\text{O}_3$ , or methyl formate,  $\text{CH}_3\text{CHO}_2$ , or grape-sugar,  $\text{C}_6\text{H}_{12}\text{O}_6$ .

4. Give the formula and percentage composition of common alcohol.

Formula,  $\text{C}_2\text{H}_6\text{O}$ .

C, 24	46 : 100 :: 24 :	percentage of carbon.
H, 6	46 : 100 :: 6 :	percentage of hydrogen.
O 16	46 : 100 :: 16 :	percentage of oxygen.
46		

Whence—

Carbon, .....	52.18
Hydrogen, .....	13.04
Oxygen, .....	34.78
	<hr/> 100.00

5. Under what circumstances does marsh gas occur in nature, and how can you prepare it artificially?

See p. 42.

6. Give the symbolic and graphic formulæ of the following compounds:—formic acid, acetic acid, oxalic acid, marsh gas, methyl, chloroform, ether.

Name.	Symbolic Formula.	Graphic Formula.
Formic acid,	$\begin{Bmatrix} \text{H} \\ \text{C} \\ \text{COH} \end{Bmatrix}$	

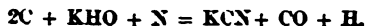
Common Name	Chemical Formula	Graphic Formula
Formic acid	$\text{CH}_2\text{O}_2$	$\begin{array}{c} \text{H} \\   \\ \text{C} - \text{O} - \text{H} \\   \\ \text{O} \end{array}$
Acetic acid	$\text{C}_2\text{H}_4\text{O}_2$	$\begin{array}{c} \text{H} \quad \text{O} \\   \quad // \\ \text{C} - \text{C} - \text{O} - \text{H} \\   \quad   \\ \text{O} \quad \text{H} \end{array}$
Propionic acid	$\text{C}_3\text{H}_6\text{O}_2$	$\begin{array}{c} \text{H} \quad \text{O} \\   \quad // \\ \text{C} - \text{C} - \text{C} - \text{O} - \text{H} \\   \quad   \quad   \\ \text{O} \quad \text{H} \quad \text{H} \end{array}$
Butyric acid	$\text{C}_4\text{H}_8\text{O}_2$	$\begin{array}{c} \text{H} \quad \text{O} \\   \quad // \\ \text{C} - \text{C} - \text{C} - \text{C} - \text{O} - \text{H} \\   \quad   \quad   \quad   \\ \text{O} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$
Valeric acid	$\text{C}_5\text{H}_{10}\text{O}_2$	$\begin{array}{c} \text{H} \quad \text{O} \\   \quad // \\ \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{O} - \text{H} \\   \quad   \quad   \quad   \quad   \\ \text{O} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$
Caproic acid	$\text{C}_6\text{H}_{12}\text{O}_2$	$\begin{array}{c} \text{H} \quad \text{O} \\   \quad // \\ \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{O} - \text{H} \\   \quad   \quad   \quad   \quad   \quad   \\ \text{O} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$
Heptic acid	$\text{C}_7\text{H}_{14}\text{O}_2$	$\begin{array}{c} \text{H} \quad \text{O} \\   \quad // \\ \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{O} - \text{H} \\   \quad   \quad   \quad   \quad   \quad   \quad   \\ \text{O} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$
Octic acid	$\text{C}_8\text{H}_{16}\text{O}_2$	$\begin{array}{c} \text{H} \quad \text{O} \\   \quad // \\ \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{O} - \text{H} \\   \quad   \quad   \quad   \quad   \quad   \quad   \quad   \\ \text{O} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$

7. Describe the preparation and properties of the compound neutral steryl.

See p. 28.

8. Some charcoal and caustic potash are given to you, and you are required to make prussic acid and oxalic acid: how will you proceed?

Neither of the problems proposed is capable of solution with only the materials given, but the answer expected is probably the following. If the charcoal be mixed with the caustic potash, and heated in a tube to redness, while nitrogen gas is passed through the tube, potassium cyanide will be formed—

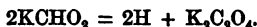


If this potassium cyanide be distilled with a dilute acid, prussic acid will be obtained, as described on p. 48.

By boiling prussic acid with caustic potash, potassium formiate will be formed, as mentioned p. 48.



And by heating potassium formiate by itself it is converted into potassium oxalate, with evolution of hydrogen, (see p. 37.)—

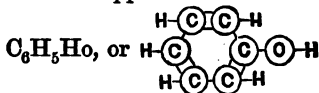


If this potassium oxalate be dissolved in water and solution of calcium chloride added, a precipitate of calcium oxalate will be obtained, which may be collected on a filter and washed. If then the precipitate be mixed with dilute sulphuric acid, and the clear liquid be poured off and evaporated, oxalic acid will crystallize out.

9. Describe minutely how you would prepare ethylic iodide (iodide of ethyl).

See p. 63.

10. What is the formula of phenylic alcohol or carbolic acid, whence is it obtained, and to what useful purposes has it been applied?

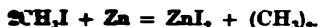


Carbolic acid is obtained from the oil obtained as a by-product in the manufacture of coal gas—the heavy coal-tar oil. See p. 58.

It is employed as a disinfectant and to prevent the decay of wood, and in the pure state in medicine.

11. How are the monad positive radicals extracted from their iodides, and from the acids of the acetic series?

The monad positive radicals are extracted from their iodides by heating together with zinc in closed tubes. Thus, methyl iodide yields the radical methyl—



They are obtained from the acids of the acetic series by anionic decomposition. Thus, if a concentrated solution of potassium acetate be subjected to electrolysis, the acid decomposed into carbon dioxide, hydrogen, and methyl-



In like manner butyric acid yields propyl—



See p. 28.

12. What is the composition of acetic ether, and how would you prepare this substance?

See also p. 79.

## 1870.

1. Give the formulæ and percentage composition of formic acid and oxalic acid.

Formic acid,  $\text{CH}_2\text{O}_2$ .

C	12	46 : 100 :: 12 :	percentage of carbon.
H <sub>2</sub>	2	46 : 100 :: 2 :	percentage of hydrogen.
O <sub>2</sub>	32	46 : 100 :: 32 :	percentage of oxygen.
	<u>46</u>		

Whence—

Carbon	26.09
Hydrogen	4.35
Oxygen	69.56
	<u>100.00</u>

Oxalic acid,  $\text{C}_2\text{H}_2\text{O}_4$ .

C <sub>2</sub>	24	90 : 100 :: 24 :	percentage of carbon.
H <sub>2</sub>	2	90 : 100 :: 2 :	percentage of hydrogen.
O <sub>4</sub>	64	90 : 100 :: 64 :	percentage of oxygen.
	<u>90</u>		



following substances:—Prussic acid, acetic acid, alcohol, methyl, and marsh gas—

Name.	Symbolic Formula.	Graphic Formula.
Prussic acid,.....	$\left\{ \begin{array}{l} \text{CN}''' \\ \text{H} \end{array} \right.$	$\text{H}-\text{C} \equiv \text{N}$
Acetic acid,.....	$\left. \begin{array}{l} \\ \\ \end{array} \right\}$ see Question 6. 1869.	
Methyl,.....		
Marsh Gas,.....		
Alcohol,.....	$\left\{ \begin{array}{l} \text{CH}_3 \\ \text{CH}_2\text{Ho} \end{array} \right.$	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{Cl} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$

5. What member of the alcohol family is found among the products of the destructive distillation of wood; how can you extract it in a state of purity from wood naphtha, and what is its graphic formula?

Methyl alcohol—wood naphtha—is the crude methyl alcohol, from which the pure substance is best extracted by distilling the wood naphtha with sulphuric acid and potassium binoxalate, so as to obtain methyl oxalate, and then decomposing this by distilling it with water, as described p. 78.

6. How can you detect the presence of nitrogen in an organic substance?

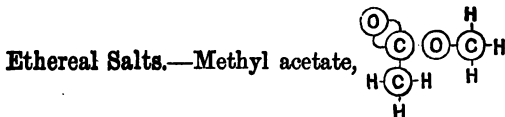
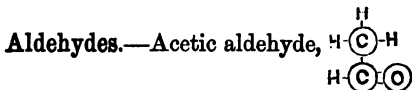
By the methods described pp. 15 and 16.

7. You are required to make 1 oz. of lactic acid from milk; how will you do it?

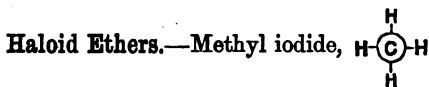
By allowing the milk to become sour, then adding excess of zinc oxide, filtering, and evaporating, by which zinc lactate will be obtained. From the zinc lactate the acid is to be extracted, as described p. 78.

8. Give the name and graphic formula of a member of each of the following families of organic compounds:—Alcohols, aldehydes, ethereal salts, ethers, and haloid ethers.

**Alcohols.**—Common alcohol, formula given above, Question 4.



**Ethers.**—Common ether, formula given above, Question 6, 1869.



9. If a mixture of acetate of potash, caustic soda, and quicklime be heated to a temperature somewhat below redness, what gaseous product is obtained? Give its name and formula, and state where it is met with in nature.

Marsh gas, or methyl hydride,  $\text{CH}_4$ .

In the gas which rises from the decomposing vegetable matter at the bottoms of marshes, and in the fire damp which collects in coal mines.

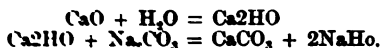
10. You have given to you the following materials, and are required to make acetic acid; state exactly what operations you will perform, and explain all chemical changes by equations:—

Ethyl iodide.  
Sodic carbonate.  
Quicklime.

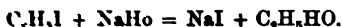
Water.  
Potassic chromate.  
Sulphuric acid.

The first operation is to prepare caustic soda, for which purpose a moderately dilute solution of the sodium carbonate must be boiled with the lime, then the calcium carbonate allowed to settle, and the clear solution of

caustic soda decanted off and concentrated by evaporation. The decomposition is represented by the equations—



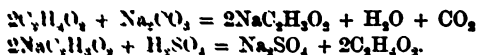
The strong caustic soda solution is then distilled with the ethyl iodide in a retort. The distillate contains alcohol—



The distillate is now acidulated with sulphuric acid and poured on the potassic chromate in another retort and distilled again. The distillate now contains acetic acid—



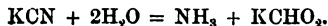
To the distillate is now added sodium carbonate till carbon dioxide ceases to be evolved, the solution is evaporated to dryness, and the dry residue once more distilled with concentrated sulphuric acid, when acetic acid distils over. The equations are—



*N.B.*— Such a question as this should be avoided. It carries only the same number of marks as question 3, for example, although a correct answer to it is worth at least three times as much as a correct answer to No. 3. But what is more important is, that it is easily possible to secure full marks for answers to Nos. 1 and 3, while in this question the chances are greatly against obtaining full marks, as there are so many opportunities of making mistakes. The eight questions to be selected in this paper are obviously Nos. 1, 2, 3, 4, 5, 8, 9, and 11.

11. If an alkaline solution of potassic cyanide be boiled, what decomposition takes place?

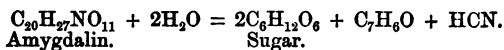
Potassium formiate is produced and ammonia is given off—



12. If bitter almonds be macerated in warm water, what member of the aldehyde family is produced; and why is this aldehyde not formed when sweet are substituted for bitter almonds?

Bitter almond oil, or benzoic aldehyde,  $\left\{ \begin{array}{l} \text{C}^{\bullet}\text{OH}. \\ \text{C}_6\text{H}_5 \end{array} \right.$

Benzoic aldehyde is not contained ready formed in bitter almonds, but is produced by a peculiar fermentation which takes place when the kernels are bruised in water. Bitter almonds contain a substance called *amygdalin*, which, under the action of the peculiar ferment—*emulsin*, also contained in the almonds—breaks up into benzoic aldehyde, hydrocyanic acid, and sugar, as shown in the equation—



Amygdalin is not contained in sweet almonds, which therefore do not yield benzoic aldehyde.

1871.

#### INSTRUCTIONS.

You are only permitted to attempt *eight* questions. Of these, two must be the first two on the paper, and if you are coming up under § XXXIX. of the Science Directory for a laboratory grant, you must attempt Question 3. With these exceptions, you may select the Questions from any part of the paper.

Atomic weights to be used:—

H	=	1
O	=	16
C	=	12
Cl	=	35.5
N	=	14
Pt	=	197.4

1. Describe the preparation of ethylic cyanide.

See p. 64.

2. You have given to you some potash, charcoal, and sulphuric acid, and are required to prepare hydrocyanic acid: how will you do it?

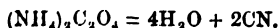
See answer to Question 8 of 1869.

3. You are required to analyze a mixture containing potassic formiate, calcic oxalate, and hydric potassic tartrate. Describe how you will identify the organic acids present in this mixture.

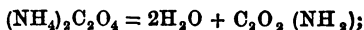
By treatment with water, the potassic formiate will be dissolved, whilst the other two salts will remain behind. The filtrate may be concentrated by evaporation, and the formic acid recognized by the following reactions:—(a.) If boiled with concentrated sulphuric acid, carbonic oxide will be evolved, which will burn at the mouth of the tube with a blue flame. (b.) If boiled with a solution of silver nitrate, the silver will be reduced to the metallic state. The residue, containing the oxalate and tartrate, may be treated with a cold solution of caustic potash, which dissolves the hydric potassic tartrate, but leaves the calcic oxalate. The tartaric acid in the filtrate may be detected by the charring and characteristic odour produced by warming with sulphuric acid. The calcium oxalate left behind may be recognized by the following two tests:—(a.) The production of calcium carbonate by ignition to redness; (b.) The evolution of carbonic anhydride on treatment with a dilute acid and manganese dioxide.

4. How can oxatyl (oxalic acid) be converted into cynnogen, and *vice versa*?

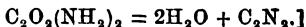
By saturating it with ammonia, so as to form ammonium oxalate; and then by heating this with phosphoric pentoxide, so as to abstract water from it—



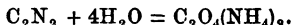
[Strictly, the decomposition would be effected in two stages—ammonium oxalate, heated by itself, loses water, and gives *oxamide*,  $\left\{ \begin{array}{l} \text{CO}(\text{NH}_2) \\ \text{CO}(\text{NH}_2) \end{array} \right\}$ —



and oxamide, heated with phosphoric anhydride, gives cyanogen—



The opposite decomposition occurs when an aqueous solution of cyanogen gas is kept. It is found after a time to contain ammonium oxalate—



5. What reaction occurs when ethylic cyanide is boiled with a solution of caustic potash?

Potassium propionate is formed, and ammonia given off, according to the equation—



6. The double salt formed by hydrochlorate of morphine and platinic chloride, yields on ignition 20·14 per cent. of platinum. Calculate the molecular weight of morphine.

This is a question on a subject distinctly not included in the syllabus, and which therefore ought not to have been proposed. The syllabus says nothing either of the calculation of molecular formula, nor of the alkaloids; and it is difficult to see how the candidate can be expected to know what sort of formulæ this double salt possesses. The answer, however, is as follows:—Morphia is a substance belonging to the *alkaloids*, which are substances containing nitrogen, and to some extent resembling ammonia in properties. They form salts with hydrochloric acid, which, like ammonium chloride, give precipitates with platinum chloride. These precipitates are decomposed on heating to redness, leaving be

hind nothing but platinum. Suppose we assign to such an alkaloid the formula  $C_2H_5N_2O_4$ , then the formula of the hydrochlorate will be  $C_2H_5N_2O_4HCl$ , and that of the double salt  $(C_2H_5N_2O_4HCl)_2PtCl_4$ , corresponding to  $(NH_4HCl)_2PtCl_4$ . If we calculate the molecular weight of the whole compound by the proportion

$$20.14 : 197.4 :: 100 :$$

we obtain 980.1 as result. If now we subtract from this the atomic weight of  $PtCl_4$ —viz., 339.4, and divide the remainder by 2, we obtain 320.35, which is the molecular weight of  $C_2H_5N_2O_4HCl$ . Subtracting from this 36.5, we obtain 283.85, which is the result required. The exact molecular weight of morphia is 285, as its formula is  $C_{17}H_{19}NO_3$ .

7. Give the name and graphic formula of a member of each of the following families of organic compounds:—Monad positive radicals, monad negative radicals, haloid ethers, and monobasic acids.

**Monad Positive Radicals.**—Methyl, formula given, Question 6, 1869.

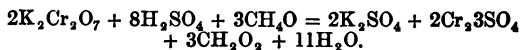
**Monad Negative Radicals.**—Oxalic acid, formula given, Question 6, 1869.

**Haloid Ethers.**—Methyl iodide, formula given, Question 8, 1870.

**Monobasic Acids.**—Formic acid, formula given, Question 6, 1869.

8. What takes place when methylic alcohol is added to a boiling solution of red potassic chromate acidified with sulphuric acid?

Formic acid is obtained—



9. How is phenylic alcohol manufactured, and what are its properties and uses?

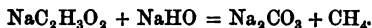
See answer to Question 10, 1869.

10. You have given to you the following materials, and are required to make methylic hydride or marsh gas. State concisely what operations you will perform, and explain all chemical changes by equations :—

Alcohol.  
Sodic carbonate.  
Quicklime.

Water.  
Potassic chromate.  
Sulphuric acid.

Sodium acetate would be prepared from the alcohol exactly as described in the answer to Question 10 of 1870. Then this would be heated to redness, with a mixture of lime and caustic soda (see p. 42)—



11. An organic compound yielded on analysis the following results :—

Carbon, .....	23·76
Hydrogen, .....	5·94
Chlorine, .....	70·30
	<hr/>
	100·00

Give the empirical formula of the compound.

$$\begin{array}{lcl} \text{C} & 23\cdot76 \div 12 & = 1\cdot98 \\ \text{H} & 5\cdot94 \div 1 & = 5\cdot94 \\ \text{Cl} & 70\cdot30 \div 35\cdot5 & = 1\cdot98 \end{array}$$

Formula required,  $\text{CH}_3\text{Cl}$ , or methyl chloride.

12. How would you experimentally determine the percentage of nitrogen in quinine?

By the method described, p. 15.

1872.

## INSTRUCTIONS.

You are only permitted to attempt eight questions. Of these, two must be the first two on the paper, and if you are coming up under Section XLIV. of the Science Directory for an extra payment, you must attempt Question 3. With these exceptions, you may select the questions from any part of the paper.

Atomic weights to be used—

$$\begin{aligned} \text{H} &= 1 \\ \text{C} &= 16 \\ \text{O} &= 12 \\ \text{Cl} &= 35.5 \end{aligned}$$

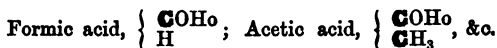

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1. Describe a process for the preparation of the radical ethyl.

See p. 28.

2. Define an organic acid; and state what acid is produced when ethylic alcohol is boiled with a mixture of potassic chromate and dilute sulphuric acid.

An organic acid is a compound of one or more atoms of the group  $\text{COHo}$ , or oxatyl, with hydrogen or an organic radical, as—



Acetic acid is produced by boiling ethyl alcohol with potassic chromate and sulphuric acid.

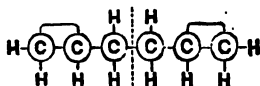
3. You are required to prepare pure cyanogen, and to fill a small glass cylinder with it. Describe minutely how

you will do it ; make a sketch of the apparatus, and show the nature of the chemical reaction by an equation.

See p. 35.

4. Give the name and graphic formula of a member of each of the following families of organic compounds :—  
Monad radicals of the vinyl series, hydrides of the monad positive radicals, the alcohols and the aldehydes.

**Monad Radicals of the Vinyl Series.**—Allyl,.....



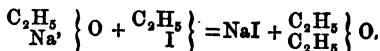
**Hydrides of the Monad Positive Radicals.**—Methyl hydride. Question 6, 1869.

**Alcohols.**—Common alcohol. Question 8, 1870.

**Aldehydes.**—Acetic aldehyde. Question 8, 1870.

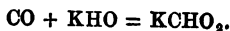
5. Give the name and formula of the volatile compound which is formed when ethylic iodide is digested with sodic ethylate. Show the reaction by an equation.

Ether,  $\left. \begin{array}{l} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \right\} \text{O}.$



6. What organic compound is formed by the prolonged action, at 100° C., of potassic hydrate upon carbonic oxide? Express the chemical change by an equation.

Potassium formate.



7. You have given to you the following materials, from which you are required to make lactic acid—

Sugar.	Zinc carbonate.	Chalk.
Tartaric acid.	Water.	Sulphuric acid.
Decayed cheese.	Milk.	Ferrous sulphide.

Describe the necessary processes.

The process is described p. 77.

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ing. It may be further recognized by its blackening with sulphuric acid. The calcium oxalate is recognized by evolving carbon dioxide when treated with a dilute acid and manganese dioxide.

11. Describe the analytical process for the determination of carbon and hydrogen in an organic compound.

See p. 12.

12. Give the formulæ and percentage composition of cyanogen and benzol.

Cyanogen,  $C_2N_2$ .

$C_2$	24	52 : 100 :: 24 : percentage of carbon.
$N_2$	28	52 : 100 :: 28 : percentage of nitrogen.
	<hr/> 52	

Whence—

Carbon, .....	46.15
Nitrogen, .....	53.85
	<hr/> 100.00

Benzol,  $C_6H_6$ .

$C_6$	72	78 : 100 :: 72 : percentage of carbon.
$H_6$	6	78 : 100 :: 6 : percentage of hydrogen.
	<hr/> 78	

Whence—

Carbon, .....	92.31
Hydrogen, .....	7.69
	<hr/> 100.00



## EXERCISES.

---

1. Find the formulæ of the substances possessing the following percentage composition :—

(a.)	Carbon, .....	29·02
	Hydrogen, .....	4·15
	Oxygen, .....	39·80
	Zinc, .....	27·03
		<hr/>
		100·00
(b.)	Carbon, .....	62·07
	Hydrogen, .....	10·34
	Oxygen, .....	27·59
		<hr/>
		100·00
(c.)	Carbon, .....	25·52
	Hydrogen, .....	2·66
	Oxygen, .....	51·03
	Potassium, .....	20·79
		<hr/>
		100·00
(d.)	Carbon, .....	77·42
	Hydrogen, .....	7·53
	Nitrogen, .....	15·05
		<hr/>
		100·00
(e.)	Carbon, .....	65·46
	Hydrogen, .....	9·09
	Nitrogen, .....	25·45
		<hr/>
		100·00

2. Required the formulæ of substances which give the following results on analysis:—

- (a.) 0·414 gr. substance gave 0·396 gr.  $\text{CO}_2$ , and 0·162 gr.  $\text{H}_2\text{O}$ .

(b.) 0.4107 gr. substance gave 1.0369 gr.  $\text{CO}_2$ , and 0.1818 gr.  $\text{H}_2\text{O}$ .

(c.) 0.3762 gr. substance gave 0.5808 gr.  $\text{CO}_2$ , and 0.2178 gr.  $\text{H}_2\text{O}$ .

3. A substance containing carbon, hydrogen, and oxygen yielded the following numbers on analysis. Required its formula—

0.602 gr. substance gave 0.821 gr.  $\text{CO}_2$ , and 0.42 gr.  $\text{H}_2\text{O}$ .

1.29 gr. substance gave 2.47 gr.  $\text{AgCl}$ .

4. 0.68 of an organic base gave, on combustion, 1.76 gr.  $\text{CO}_2$ , and 0.792 gr.  $\text{H}_2\text{O}$ ; 0.832 gr. of the platinum double salt left behind on heating to redness, 0.282 gr. metallic platinum. Find the formula of the base.

5. Find the vapour density (in reference to hydrogen) of a substance from the following data:—

Weight of balloon and air, .....	17.3056 gr.
Weight of balloon and vapour, .....	17.3977 gr.
Temperature of weighing, .....	15° C.
Barometer, .....	755.
Temperature at sealing, .....	150° C.
Capacity of balloon, .....	125 c.c.

6. Find the rational formula of a liquid from the following data:—

(a.) Analysis—

0.461 gr. gave 1.094  $\text{CO}_2$  and 0.554 gr.  $\text{H}_2\text{O}$ .

(b.) Determination of vapour density—

Weight of globe and air at 16° C. .... 20.2578 gr.

    "          " filled with vapour at 167°, 20.4100 gr.

Capacity of globe, ..... 171.5 c.c.

(c.) On oxidation it yielded an acid, the silver salt of which was analysed—

0.222 gr. left, on ignition, 0.1230 gr. metallic silver.

7. Required the formula of a substance yielding the following analytical results:—

0.221 gr. heated with lime gave 0.215 gr. AgCl.  
 0.337 gr. on combustion gave 0.794 gr.  $\text{CO}_2$  and 0.355 gr.  $\text{H}_2\text{O}$ .

8. Required the formula of an organic iodide, which yielded on analysis the following data:—

- (a.) 0.3060 gr. gave 0.2412 gr.  $\text{CO}_2$  and 0.1134 gr.  $\text{H}_2\text{O}$ .  
 (b.) 0.3162 gr. gave 0.4434 gr. AgI.

9. A saturated hydrocarbon, which contained 83.93 per cent. of C and 16.13 per cent. of H, gave the following numbers:—

Balloon and air at $11^\circ \text{C}$ .....	40.7955.
Balloon and vapour,.....	41.0960.
Temp. of sealing,.....	$173^\circ \text{C}$ .
Capacity of balloon,.....	189 c.c.

Required the formula of the substance.

10. Find the formula of an acid, the silver salt of which contains—

Carbon,.....	13.79
Hydrogen,.....	1.15
Oxygen,.....	18.39
Silver oxide,.....	66.67
	<hr/>
	100.00

11. Find the formula of strychnine from the following analysis of its hydrochlorate—

Carbon,.....	68.02
Hydrogen,.....	6.21
Nitrogen,.....	7.56
Oxygen,.....	8.64
Chlorine,.....	9.57
	<hr/>
	100.00

12. What is the formula of a substance which gave the following results on analysis?

0.154 gr. gave 0.308 gr.  $\text{CO}_2$  and 0.126 gr.  $\text{H}_2\text{O}$ .

On oxidation it yielded an acid, the silver salt of which contained 64.68 per cent. of silver.

## ANSWERS.

1. (a.) Zinc lactate,  $\text{Zn}2\text{C}_3\text{H}_5\text{O}_3$ .  
 (b.) Butyric ether,  $\text{C}_3\text{H}_6\text{O}$ .  
 (c.) Potassium hydrogen tartrate,  $\text{KHC}_4\text{H}_4\text{O}_6$ .  
 (d.) Aniline,  $\text{C}_6\text{H}_7\text{N}$ .  
 (e.) Ethyl cyanide,  $\text{C}_3\text{H}_5\text{N}$ .
2. (a.)  $\text{CH}_2\text{O}_2$ , formic acid.  
 (b.)  $\text{C}_7\text{H}_6\text{O}_2$ , benzoic acid.  
 (c.)  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , sugar.
3.  $\text{C}_2\text{H}_5\text{Cl}$ , ethyl chloride.
4.  $\text{C}_6\text{H}_{11}\text{N}$ , piperidine.
5. 35.
6.  $\text{C}_4\text{H}_{10}\text{O}$ , butyl alcohol.
7.  $\text{C}_8\text{H}_{17}\text{Cl}$ , octyl chloride.
8.  $\text{C}_3\text{H}_7\text{I}$ , propyl iodide.
9.  $\text{C}_7\text{H}_{16}$ , heptyl hydride,
10.  $\text{C}_4\text{H}_6\text{O}_5$ , malic acid.
11.  $\text{C}_8\text{H}_{17}\text{N}_2\text{O}_2$ , strychnine.
12.  $\text{C}_2\text{H}_4\text{O}$ , aldehyde.







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